CRANFIELD UNIVERSITY

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DEVELOPMENT OF IMPROVED METHODS FOR THE CHARACTERISATION OF ORGANIC CHEMICALS EMITTED INTO INDOOR AIR BY BUILDING AND FURNISHING PRODUCTS

Cranfield Health

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Supervisor: Dr Derrick R Crump

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ABSTRACT

A wide range of organic compounds are released from building and furnishing products and these have the potential to adversely affect indoor air quality. There are growing international requirements for testing and controlling these emissions for the protection of public health. The test methods require specialist analytical chemistry facilities based on thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). This project has addressed the need for better performance and greater automation of the analysis, as well as development of simpler screening tests.

A variety of products were tested using screening techniques, with an emission cell method being used as a reference test. Short duration tests, using a micro-scale chamber at slightly elevated temperature, were shown to have the potential to predict emissions occurring during longer term reference tests.

Multi-sorbent air sampling tubes, that have the potential to extend the volatility range of compounds determined by a single TD/GC/MS analysis, were compared with Tenax TA tubes specified by current standard methods. This showed no difference in performance for the range of compounds for which Tenax is optimal, with improved performance for a number of more volatile compounds.

The determination of formaldehyde was investigated using 2-hydroxymethylpiperidine as a derivatising agent, followed by TD/GC/MS. The results showed the possibility of this method being developed as an alternative to the current standard method that involves solvent elution and liquid chromatography.

The performance of a newly developed time-of-flight mass spectrometer was compared with a standard quadrupole instrument. This showed its potential, with the use of re-collection, to extend the concentration range of compounds quantified from a single air sample, of particular benefit for the determination of carcinogens.

New compound identification software was applied to increase automation of analysis of the TD/GC/MS data. Good correlation with manual processing was achieved, demonstrating the possibility of routine application to material emissions testing.

Keywords:

VOCs, VVOCs, SVOCs, formaldehyde, screening tests, Tenax, multi-sorbent, material emissions, thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS), time-of-flight (TOF) MS, TargetView software.

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DECLARATION

This is a declaration to certify that:

(a) except as specifically stated, the contents of this thesis represent solely my own work

(b) the thesis has not been submitted for any other academic or professional award

(c) the thesis is submitted on the conditions contained in the regulations

(d) the work was carried out as part of my period of study and not previously or subsequently

The results detailed in Section 4.3.2 are intended for publication under joint names (drafted for submission to Journal of Chromatography A) and parts of the results detailed in Chapter 5 have contributed to a joint publication in Analytical Methods (2013, 5, 2746-2756). Other results from the project have contributed to joint papers published in the proceedings of the Indoor Air Conference 2011, Austin, Texas, the Healthy Buildings Conference 2012, Brisbane, Australia and the Annual UK Review Meetings on Outdoor and Indoor Air Pollution Research, 2011 and 2012, Cranfield. Details of these papers are contained in Appendix G of this thesis.

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LIST OF NOMENCLATURE/ABBREVIATIONS

12-DCE	1,2-Dichloroethane
123-TMB	1,2,3-Trimethylbenzene
13-DCP	1,3-Dichloropropan-2-ol
2-BE	2-Butoxyethanol
2-EHA	2-Ethylhexanoic acid
2-HMP	2-Hydroxymethylpiperidine
4-PCH	4-Phenylcyclohexene
µg m^{-3}	Micrograms per cubic metre
µ-CTE	Micro-Chamber/Thermal Extractor
ACGIH	American Conference of Governmental Industrial Hygienists
AFSSET	Agence francaise de securite sanitaire de l-environnement et du travail (French Agency for Environmental and Occupational Health and Safety)
AgBB	Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (Committee for Health-related Evaluation of Building Products)
AMDIS	Automated Mass Spectral Deconvolution and Identification System
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BAM	BAM Federal Institute for Materials Research and Testing
BHT	Butylated hydroxytoluene (2,6-di-tert-butyl-4-methylphenol)
BIFMA	Business and Institutional Furniture Manufacturers Association International
CalEPA	California Environmental Protection Agency
Cal01350	Standard Practice for the Testing of Volatile Organic Emissions from Various Sources Using Small-Scale Environmental Chambers (California)
CDPH	California Department of Public Health
CEN	Comite Europeen de Normalisation (European Committee for Standardisation)
CMR	Carcinogenic, mutagenic or reprotoxic
COMEAP	Committee on the Medical Effects of Air Pollutants (UK)
COSHH	Control of substances hazardous to health
CPD	Construction Products Directive
CPR	Constructions Products Regulation
CREL	Chronic Reference Exposure Level
CWA	Chemical Warfare Agent
DBC	Dynamic Background Compensation
DBP	Dibutyl phthalate
DICL	Danish Indoor Climate Label

DEHP	Di-2-ethylhexyl phthalate
DEHT	Di-2-ethylhexyl terephthalate
DINP	Diisononyl phthalate
DNPH	2,4-dinitrophenylhydrazine
EC	European Commission
ECA	European Collaborative Action
EGDS	Expert Group on Dangerous Substances
EU	European Union
FID	Flame ionisation detector
FLEC	Field and Laboratory Emission Cell
FO	Formaldehyde oxazolidine
GC	Gas chromatograph/gas chromatography
GEI	Greenguard Environmental Institute
GUT	Gemeinschaft umweltfreundlicher Teppichboden [translation is Association of Environmentally Friendly Carpets]
HMCTS	Hexamethylcyclotrisiloxane
HPLC	High performance liquid chromatography
HSE	Health and Safety Executive
HSL	Health and Safety Laboratory
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
I.D.	Internal diameter
IEH	Institute of Environment and Health (Cranfield University)
IS	Internal standard
ISO	International Standards Organisation
LCI	Lowest concentration of interest
LOD	Limit of detection
LOQ	Limit of quantification
MCB	Methylcyclobutane
MFC	Mass flow controller
MIBK	Methyl isobutyl ketone (4-methylpentan-2-one)
MS	Mass spectrometer/spectrometry
MSD	Mass selective detector
m/z	Mass to charge ratio
NIOSH	National Institute for Occupational Safety and Health (USA)
NIST	National Institute of Standard and Technology (USA)
NPL	National Physical Laboratory
OEHHA	Office of Environmental Health Hazard Assessment (California)
OMCTS	Octamethylcyclotetrasiloxane
PCA	Principal component analysis

PAH	Polycyclic aromatic hydrocarbon
PFPH	Pentafluorophenyl hydrazine
POM	Particulate organic matter
PT	Proficiency testing
PU	Polyurethane
PVC	Polyvinyl chloride
PVCu	Unplasticised PVC
QC	Quality control
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RT	Retention time
SER	Area specific emission rate
SIFT	Selected ion flow tube
SIM	Selected ion monitoring
S/N	Signal to noise
SOP	Standard operating procedure
SPME	Solid phase micro-extraction
SSV	Safe sampling volume
SVOC	Semi volatile organic compound
TAC	Toxic air contaminant
TD	Thermal desorption/thermal desorber
TLV	Threshold limit value
TOF	Time of flight
TVOC(s)	Total volatile organic compound(s)
TXIB	2,2,4-Trimethylpentanedioldiisobutyrate
VOC	Volatile organic compound
VVOC	Very volatile organic compound
WHO	World Health Organization

1 INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

A wide range of organic chemicals are released from building and furnishing products and these have the potential to adversely affect indoor air quality (IAQ). People in Northern Europe typically spend 90% of their time indoors, so the indoor environment is a major determiner of exposure to air pollutants, particularly for vulnerable groups such as children, the sick and the elderly. Current concerns about climate change, resulting in mitigation measures which employ a wide range of innovative products to maximise the thermal performance of structures, along with requirements for more airtight new and renovated buildings to reduce ventilation rates, are likely to result in increased levels of indoor air pollutants.

A number of government and industry initiatives across Europe (and elsewhere) have independently developed regulatory and voluntary controls of emissions from products for the protection of public health. Methods employed typically involve testing of the material in an emissions test chamber with analysis using thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). Extensive lists of chemicals to determine are required by some authorities. International efforts are currently aiming to agree methods for evaluating the emissions obtained. Specifications under discussion within Europe challenge the current performance of methods with regards to the range of chemicals, in terms of boiling point, polarity and reactivity, to be determined. There is also the requirement to determine chemicals of high toxicity, including carcinogens, with high sensitivity.

The growing requirement for product emissions testing represents a burden for industry in terms of cost and time. Certification of products requires testing according to a reference method which takes a number of weeks for a result to be obtained. The use of simpler, quicker screening tests to complement emission chamber tests is expected to become important for quality control purposes and other in-house tests by material producers. Comparability of these screening methods with the reference method for a particular application, however, needs to be demonstrated.

The following sections describe further the range and significance of organic chemicals found in air and emitted from materials, methods which are employed for their measurement, details of the existing and proposed labelling schemes for material emissions and recent developments in analytical instrumentation. Possibilities for improvements in current methods, which form the objectives for the present project, are then identified.

1.2 Organic chemicals in indoor air

Air quality policies within Europe have mainly focussed on controlling the concentrations of pollutants in outdoor air resulting from industrial processes, traffic and generation of heat and power (Fernandes et al., 2009). While outdoor air pollution can still be an issue, indoor air pollution has more recently also been recognised as a significant cause for concern. Reasons for this are that a wide range of sources of pollutants can occur within buildings, and rates of air exchange with the outdoors can be insufficient to prevent the occurrence of elevated levels of pollutants in indoor air. Also, much of our time is spent indoors, in many parts of the world this can amount to more than 90 %, and therefore our exposure to air pollutants occurs mostly indoors (Sundell, 2004). Climate change could also have a significant effect on IAQ, as was concluded in a recent report published by the Institute of Medicine, the health arm of the National Academy of Sciences, USA (Institute of Medicine, 2011). This might result from mitigation measures, such as greater use of insulation, to reduce energy use in buildings and adaptation measures, such as increased use of air conditioning. Both of these could lead to lower ventilation rates and higher concentrations of pollutants in indoor environments. Pressures towards wider use of recycled building materials, encouraged by sustainable building schemes (Yu and Kim, 2011), could increase levels of indoor air pollutants. Changes in outdoor concentrations of pollutants due to alterations in atmospheric chemistry or atmospheric circulation could also affect indoor concentrations.

Depending on their volatility, organic chemicals in indoor air are either present in the gas phase or are bound to suspended particulate matter or deposited dust. In 1989 the World Health Organization (WHO) classified organic compounds based on boiling point (WHO, 1989) and this classification is shown in Table 1-1. Other definitions of

volatile organic compounds (VOCs) exist, but the indoor air science community widely apply the WHO classification. According to this classification, compounds with boiling points lower than ~50 to 100 ºC are described as very volatile organic compounds (VVOCs) and those with boiling points above ~240 to 260 ºC are described as semi-volatile organic compounds (SVOCs). One chemical of particular concern in indoor atmospheres, formaldehyde, the boiling point of which is -19 ºC, is therefore classified as a VVOC. Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is therefore also used as a criterion for classification of the volatility of organic chemicals. The table also includes examples of media used to sample the different ranges of compounds from the air; these are discussed in Section 1.2.4.

Table 1-1 The WHO classification of organic pollutants in indoor air (ISO 16000-5:2007)

Description	**Abbreviation**	**Boiling point range (°C)**		**Saturation vapour pressures (kPa)**	**Examples of sampling media**
		From	**To**		
Very volatile organic compounds	VVOC	<0	50 to 100	>15	Activated carbon, cooled sampling media, molecular sieves, canister method
Volatile organic compounds	VOC	50 to 100	240 to 260	$>10^{-2}$	Tenax, graphitised carbon or activated carbon
Semi-volatile organic compounds	SVOC	240 to 260	380 to 400	10^{-2} to 10^{-8}	Polyurethane foam (PUF) or XAD-2
Particulate organic matter	POM	>380			Filters

1.2.1 Sources of organic chemicals in indoor air

Uhde (2009) stated that there exists "an almost ubiquitous level of volatile organic compounds (VOCs) in indoor air" resulting from the use of materials and household products and that "several hundred different compounds have been identified". Sources of these compounds may be present in the room continuously or intermittently (BS EN ISO 16000-5:2007). All kinds of building products, furniture, and room textiles are the most important continuous sources (Brown, 2009). Intermittent sources include

household and consumer products (Ayoko, 2009), building occupants and a number of their activities, such as smoking and hobby work. Ambient air can also be a source of indoor air pollutants, although its contribution to the presence of VOCs in indoor atmospheres is generally less important. The concentration of a pollutant depends on the rate at which it is emitted, together with the rate at which it is transported into the building, and the rates at which it is scavenged by indoor surfaces, removed by indoor chemistry and diluted by ventilation (Weschler, 2009). Emissions from materials can be broken down into primary emissions, which have been defined as the "physical release of compounds which are present in a new product", and secondary emissions, which are "compounds produced by chemical reaction in the product or in the indoor environment" (Uhde and Salthammer, 2007). Examples of primary emissions include monomers from man-made polymers and terpenes from fresh wood. Emissions may also result from chemicals, such as fire retardants and mould inhibitors, which are used to treat materials. Examples of secondary emissions include those resulting from inherent decay of the material, for example chemically unstable urea-formaldehyde resins which release formaldehyde, and those from interactions, such as odorous alcohols formed from chemical degradation of floor adhesive and vinyl flooring placed on damp alkaline concrete (Fernandes et al., 2009). The level of primary emissions is highest immediately after a material has been manufactured and diminishes during the following months, while secondary emissions may increase with time and be long lasting (Sundell, 2004).

1.2.2 Health effects of organic chemicals

There has been much research undertaken into the possible contributions of organic chemicals to indoor air quality problems, though generally the effects observed after exposures to the levels of organic chemicals typically found in non-industrial indoor environments do not identify a specific causality (Molhave, 2009). The UK Committee on the medical effects of air pollutants, COMEAP, stated that "long term exposure to organic solvents can damage the nervous system, though exposure to much higher concentrations than are generally found indoors is needed to produce such effects" (COMEAP, 2004). Exposure to organic chemicals has however been associated with headaches and irritation to the eyes, nose and throat (Molhave, 1991). Some compounds

are known or suspected carcinogens (Fernandes et al., 2009), benzene, for example is a known genotoxic carcinogen. Mendell (2007) reviewed studies into associations between chemicals in indoor air and respiratory health or allergy in children, and found a number of such associations. Formaldehyde and phthalates were amongst risk factors identified most frequently. Other groups of compounds, such as aromatic and aliphatic hydrocarbons showed limited, but suggestive, evidence of such associations. Reduction in the levels of indoor air pollutants, including those of organic chemicals, also has the potential to significantly increase the productivity of workers as well as improving their health (Fisk, 1997).

1.2.3 Standards and guidelines for levels of organic chemicals in air

With regards to outdoor air pollution, within the European Union (EU) the Ambient Air Quality Directive (2008/50/EC) sets legally binding limits for a number of major air pollutants that impact on health (DEFRA, 2011). The organic compounds included in this are benzene and polynuclear aromatic hydrocarbons (PAHs). In England the directive is enforced by the Air Quality Standards Regulations 2010. The most recent Air Quality Strategy containing policies for the assessment and management of UK air quality and implementation of EU directives was published in 2007 (DEFRA, 2007). This lists objectives for particulate matter and for eight gaseous pollutants including benzene, 1,3-butadiene and PAHs.

In the UK workplace, the exposure of employees is regulated by the Health and Safety Executive (HSE) through the use of workplace exposure limits under "The Control of Substances Hazardous to Health Regulations (CoSHH), 1988". Until 2005, an annual updated version of the list of exposure limits was available from the HSE, more recently the current values are available from the HSE website (HSE, 2011). The current version contains just over 400 substances, around a half of which would be classified as VOCs (according to the WHO classification). The list provides concentrations which must not be exceeded, as a "time-weighted average", for an 8-hour working day. These values, however, are not applicable in law to non-occupational indoor environments, such as homes, where people may be present for significantly more than 8 hours a day. Also the values are not appropriate for various population groups, such as those in poor health, the elderly and the young. A reason for this in the case of children, given by Faustman

et al. (2000), was that they "receive greater chemical exposures per unit of body weight than adults and they are more susceptible to their effects because their tissues and organs are actively growing".

No air quality standards exist in the UK for non-occupational indoor environments, but Part F of the UK Building Regulations (Approved Document F), states that, as a performance criterion of the effectiveness of ventilation in dwellings, "exposure to total volatile organic compound levels should not exceed 300 μg m^{-3} averaged over 8 hours" (HM Government, 2010). Also an expert committee of the Department of Health has recommended guideline levels for five indoor air pollutants: formaldehyde, benzene, benzo[a]pyrene, nitrogen dioxide and carbon monoxide (COMEAP, 2004).

Within Europe, indoor air issues have been addressed, since 1987, by a series of reports co-ordinated by the European Commission's Joint Research Centre (JRC) on "Indoor Air Quality and its Impact on Man", renamed in 1999 "Indoor Air, Human Exposure and Urban Environment" (Fernandes et al., 2009). Over the period 2002-2005, the JRC co-ordinated the INDEX project which aimed to identify priorities for indoor air pollution (Kotzias et al., 2005). This involved establishing a list of compounds to be regulated in indoor environments together with recommendations for potential exposure limits with health impact criteria as a priority. From an initial list of 41 compounds examined, detailed assessment was undertaken of 14 compounds and five of these (formaldehyde, benzene, naphthalene, nitrogen dioxide and carbon monoxide) were assigned as high priority chemicals with potential for high indoor concentrations and uncontested health impacts. Acetaldehyde, xylenes, toluene and styrene were assigned as second priority chemicals. A further group of chemicals (ammonia, delta-limonene and alpha-pinene) were considered to require further research before a recommendation could be made.

Braubach and Kryzanowski (2009) have reviewed the development and status of World Health Organization (WHO) indoor air quality guidelines which aim to provide guidance in reducing the adverse health impacts of air pollution as a result of "expert evaluation of current scientific evidence". The first WHO guidelines, published in 1987, were applicable to ambient air quality in Europe (WHO, 1987). Twelve organic compounds were selected for evaluation. For those compounds that were not reported to

induce carcinogenic effects (or for which such data was insufficient) a threshold assumption was made and guideline values were proposed. For those compounds which are known or suspected carcinogens, for example benzene, the guidelines provided an estimate of lifetime cancer risk arising from exposure to the substance. A second edition of the guidelines was produced in 2000 (WHO) which evaluated the effects of 35 pollutants, including the same organic compounds as investigated in 1987. Guideline values recommended were separated according to whether the concern was due to odour/annoyance, carcinogenicity or otherwise.

A global update to the guidelines was produced in 2006 (WHO, 2006a) in which the use of the guidelines in risk assessment and policy development were reviewed, together with a revision of the guideline values for some inorganic pollutants only. The update recommended that the development of air quality guidelines specific to indoor air be explored. In response to this a working group met in 2006 to discuss the recommended scope and format of the WHO indoor air quality guidelines. The group agreed that the guidelines should cover some specific chemical pollutants, biological agents and indoor combustion products (WHO, 2006b). Six of the nine chemicals included on the list were organic chemicals: formaldehyde, benzene, naphthalene, halogenated compounds (tetrachloroethylene and trichloroethylene) and PAHs, especially benzo[a]pyrene. Work was undertaken on summarising the evidence on health hazards of specific chemical pollutants, as part of which the cancer and non-cancer effects of formaldehyde were reviewed (Nielsen and Wolkoff, 2010; Wolkoff and Nielsen, 2010). The indoor air quality guidelines were published at the end of 2010 (WHO, 2010) with the aim of eliminating, or reducing to a minimum, exposure to hazardous or possibly hazardous pollutants. The guidelines resulted from a comprehensive evaluation of the accumulated scientific evidence into the toxic properties and health effects of these pollutants.

1.2.4 Methods for the measurement of organic chemicals in air

1.2.4.1 Initial development of international standards

Brown (2002a) reviewed the methods for monitoring VOCs in workplace, indoor and ambient air and the preparation by the International Standards Organisation (ISO) of standards which seek to harmonise methods developed in different countries. The most

versatile methods for measuring atmospheric organic compounds involve collection on a solid sorbent and analysis by gas chromatography (GC) or GC-Mass spectrometry (MS). Sampling on a solid sorbent may be undertaken actively, using a sampling pump, or passively, by utilising the physical process of diffusion. Recovery of the collected compounds may be by solvent extraction or by thermal desorption. The relevant ISO standards at the time were as follows:

BS ISO 16200-1:2001 "Workplace air quality – Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography – Part 1: Pumped sampling method"

BS ISO 16200-2:2000 "Workplace air quality – Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography – Part 2: Diffusive sampling method"

BS EN ISO 16017-1:2001 "Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped sampling"

BS EN ISO 16017-2:2003 "Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 2: Diffusive sampling".

Solvent desorption of sorbents predates thermal desorption by some ten years, being developed principally in the occupational hygiene field, i.e. for workplace atmospheres. Solvent desorption typically employs activated charcoal as sorbent and carbon disulphide as solvent. Typically a few millilitres of solvent are used to desorb each sample, with injection of around 1 µl into the GC (i.e. about 0.1 % of the collected analyte). Thermal desorption (TD) is essentially a "gas-phase introduction technique for vapour-phase analytical systems such as GC and GC/MS" (Woolfenden, 2001). In the thermal desorber volatiles collected off-line onto sorbent tubes are transferred by the carrier gas onto a focusing trap. The precise selection of materials and conditions for the focussing trap allow the selective retention of a specific range of compounds. The focusing trap is then heated up very quickly and the volatile compounds present are injected into the GC in a small volume of vapour. If required, 100 % of the target

compounds trapped on the sorbent tube can be transferred to the GC column, though more typically a small 'split' is applied in which excess sample is vented to waste. TD therefore offers a sensitivity advantage compared to solvent desorption, which is important when the compounds of interest are present in the atmosphere in very low amounts.

For TD, the particular sorbent of choice is dependent upon the range of compounds of interest, as the tube capacity for a particular compound depends on sorbent-sorbate affinity. The breakthrough volume is the "volume of test atmosphere that can be passed through a sorbent tube before the concentration of eluting vapour reaches 5 % of the applied test concentration" (BS EN ISO 16017-1, 2001). Breakthrough volumes may be determined for particular combinations of sorbent and sorbate, but more often the mathematically related 'retention volume' is determined. As breakthrough volume varies with temperature, flow rate and humidity, to allow a suitable margin of safety, 50 % of the retention volume is defined as the 'safe sampling volume' (SSV). ISO 16017-1:2001 contains a list of retention volumes and safe sampling volumes which have been determined chromatographically for a range of chemicals and sorbents. For example, the SSV for n-hexane on the porous polymer sorbent Tenax™ TA is 3.2 litres, while the value on the carbon molecular sieve material Spherocarb (the current commercially available equivalent of which is Sulficarb™) is 2,000,000 litres.

Industry standard tubes, of dimensions ¼-inch outside diameter by 3.5-inch, can be used for pumped sampling at flow rates between 10 and 200 ml min^{-1}, the optimum flow rate being around 50 ml min^{-1}. The accuracy of a measurement relies on the correct selection of sorbent and air volume for the particular compounds of interest and also on a precise determination of the air volume (i.e. the calibration of the air sampling pump).

1.2.4.2 ISO 16000 series standards specific to indoor air

A further series of standards, relevant to the measurement of organic pollutants in indoor air developed by ISO, is the 16000 series. Several of these standards have been revised during the course of the project. The current standards are as follows:

Part 1 covers general aspects of sampling strategy (BS EN ISO 16000-1, 2006)

Parts 2 to 4 are specifically for formaldehyde and other carbonyl compounds (see below)

Part 5 describes a strategy for sampling for VOCs (BS EN ISO 16000-5, 2007)

Part 6 overlaps considerably with ISO 16017-1, but is applied specifically to indoor air or building material emissions testing. The method involves active sampling, thermal desorption and gas chromatography using MS or flame ionisation detection (FID) (BS ISO 16000-6, 2011). ISO 16000-6 specifies the sorbent Tenax TA and recommends a maximum sample size of 5 litres, and hence defines the operational limits of the compounds determined. A sample volume of 5 litres allows effective trapping of organic compounds within the volatility range of n-hexane to n-hexadecane. However, informative Annex D, added to the updated version of the standard issued in 2011, describes the use of a combination of sorbents arranged in order of increasing sorbent strength to extend the volatility range of compounds which can be determined by a single analysis (this is discussed further in Section 1.5.1). This standard also includes the determination of total VOC (TVOCs) which is defined as the sum of VOCs eluting between and including n-hexane and n-hexadecane on a non-polar capillary column and calibrated using their toluene equivalents.

Formaldehyde, due to its volatility and reactivity, cannot currently be effectively analysed by thermal desorption and GC but, because of its importance, a separate technique involving derivatisation followed by high performance liquid chromatography (HPLC) is specified in ISO 16000-3:2011 (for active sampling) and 16000-4:2011 (for diffusive sampling), with ISO 16000-2:2006 describing the sampling strategy specific for formaldehyde. The basis of these standard methods is the specific reaction of a carbonyl group with 2,4-dinitrophenylhydrazine (DNPH) in the presence of an acid to form stable derivatives which are amenable to HPLC with UV detection. For active sampling, DNPH is coated onto silica contained within a cartridge-type sampler and, for diffusive sampling, it is impregnated onto a filter contained within a badge-type sampler. If short term maximum formaldehyde concentrations are of importance, the active method should be employed, while the diffusive method is preferable for determining longer term average concentrations (Gavin et al., 1995). These methods can also be used to determine some other carbonyl compounds in air.

1.2.5 VOC measurements undertaken in indoor air

Numerous measurements of concentrations of VOCs in indoor environments have been undertaken by research groups across the world over the last 30 years. Some studies have looked specifically for the presence of particular compounds of concern and examples of some individual compounds investigated and their possible sources are given in Table 1-2. Other studies have investigated a wider range of VOCs, either to investigate a perceived problem with the atmosphere of a building (Brown et al., 1996; Brown et al., 1993) or as part of surveys of typical levels of air pollutants in indoor atmospheres.

Table 1-2 Examples of measurements of particular organic compounds of concern in indoor air

Compound	Possible source(s)	Reference
2-Ethylhexan-1-ol	Hydrolysis of phthalate from PVC flooring	Sakai et al., 2009
Glycol ethers	Liquid cleaning products, paints and surface coatings	Plaisance et al., 2009
p-Dichlorobenzene	Consumer products including moth repellents and toilet cleaners	Murayama et al., 2008
Carbon Disulphide	Contaminated waste site close to the building	Crump et al., 2008
Benzene	Outdoor air, tobacco smoke, vehicle kept in an integral garage	Crump et al., 2007; Mann et al., 2001
Hexachlorobutadiene	Contaminated waste site close to the building	Crump et al., 2002
Tetrachloroethylene	Dry cleaning facility close to the building	Chiappini et al., 2008
Formaldehyde	Wood-based flooring and furnishings, textiles, combustion products	Gunnarsen et al., 2008; Crump et al., 2005
Naphthalene	Damp proof membrane containing coal tar	Brown et al., 1990

An overview of the VOC concentrations found in indoor air in many countries was given by Brown et al. (1994). The compounds mostly belong to one of the following chemical classes: aliphatic hydrocarbons such as alkanes and cycloalkanes, aromatic hydrocarbons, terpenes, aldehydes, ketones, alcohols, alkoxyalcohols, esters, ethers, and halocarbons. This listing does not include a number of groups of compounds such as carboxylic acids, isocyanates or amines. Although these VOCs may be present in an indoor atmosphere they will not readily be detected with the analytical methods

routinely applied for VOCs. Correct determination of these 'special' VOCs, which may also include a number of polar compounds, requires more complex analytical work (ISO 16000-5:2007). This may involve use of a different GC column, detector or possibly, as for formaldehyde, solvent desorption and HPLC. Despite this requirement for a separate sampling and analytical method, formaldehyde is often determined as part of surveys of indoor air pollutants, due to its particular toxicity and continuing occurrence in indoor air. Details of some significant surveys of VOCs and formaldehyde (HCHO) levels in the air of homes in different countries are given in Table 1-3.

A review by Weschler (2009) summarised "changes in indoor pollutants since the 1950's". He found that levels of some indoor pollutants, such as formaldehyde and aromatic chlorinated solvents, had first increased then decreased over this time, whilst those of other chemicals, such as phthalate esters, had increased and remained high. He concluded that these changes were due to major differences in the building materials and consumer products used within buildings, with growing uses of products including polymeric flooring, synthetic carpets, foam cushioning, composite-wood, and scented cleaning agents. A further review, specifically of formaldehyde in the environment, by Salthammer et al., (2010) also noted a trend towards lower concentrations of formaldehyde over recent decades, as a result of progress made with indoor products with reduced emissions. They observed, however, that average concentrations reported "do not take into account the higher exposure which may result from new buildings or peak concentrations and individual cases". Also, the effect of lower emitting products may be counteracted by reduction in the air exchange rate in houses as a means of conservation of energy, so that there will be a continuing need for the measurement of formaldehyde concentrations indoors.

Table 1-3 Examples of surveys of VOC and formaldehyde levels in indoor air

Country	Techniques	Details/Findings	Reference
Germany (GERES)	Diffusive sampling, VOCs and formaldehyde	First survey, of 500 homes, undertaken in 1985/86. A further survey, of 579 homes of 3-14 year old children, undertaken in 2003/2006, all seasons, to investigate changes in levels over time.	Heinzow and Sagunski, 2009; Schulz et al., 2012
England (IAQ survey of England)	Diffusive sampling, VOCs: Tenax and TD/GC/MS, formaldehyde: DNPH/HPLC	876 homes, typically 150-200 VOCs detected in each home. VOC levels higher when painting had been undertaken and in newer homes, formaldehyde levels higher in newer homes and those with particleboard flooring.	Raw et al., 2004
France (French IAQ survey)	Diffusive sampling, VOCs: Carbograph and TD/GC/MS, formaldehyde: DNPH/HPLC	Initial 90 homes - levels generally low, but a wide range of values. Benzene, toluene, xylenes, alkanes, aldehydes and terpenes ubiquitous in homes investigated. Later (2003-2004), 567 dwellings (370 winter, others summer).	Kirchner et al., 2003; Billionnet et al., 2011
Australia	Active sampling, VOCs: multi-sorbent and TD/GC/MS, formaldehyde: chromotropic acid	27 established and 4 new/refurbished homes, VOC levels in established buildings generally low, with a small spread of values, but VOC levels significantly "higher in new and refurbished buildings" and did not decline to 'normal' levels "for several weeks to months".	Brown, 2002b
Sweden	Diffusive sampling, VOCs: Tenax and TD/GC/MS	178 homes, about 120 VOCs identified in the air, most of which occurred at low levels. Chemicals found included alkanes, alkenes, terpenes, aromatics, alcohols, aldehydes and ketones.	Bornehag and Stridh, 2000
11 European cities (AIRMEX)	VOCs and aldehydes	2003-2008, 182 workplaces - public buildings (including schools), 103 homes, 148 adults. Sampled summer or winter.	Kotzias et al., 2009
EXPOLIS	VOCs and aldehydes	1996-2000, 6 European cities, 50-200 adults in each city, aged 25-55 years, personal sampling and indoor and outdoor air.	Jantunen et al., 1998

1.3 Emissions of VOCs from materials

Due to the importance of materials in contributing to the organic chemicals present in indoor atmospheres, the testing of emissions from materials to be used in buildings has

become an area of growing importance (Wilke et al., 2011b; Wiegner et al., 2011; Gall et al., 2011; Salem et al., 2011). There is now also an increasing interest in the measurement of emissions from consumer products. A driver for this is the European 'REACH' regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals), which came into force on 1st June 2007 and includes "intentional and unintentional release of chemicals from 'articles' and preparations" (Woolfenden, 2009). Examples of consumer products which are known to be significant sources of exposure to VOCs are air fresheners and cleaning products (Nazaroff and Weschler, 2004). Products for which emissions tests have recently been reported are air fresheners (Uhde et al., 2011), incense and candles (Manoukian et al., 2011; Silva et al., 2011), scented children's toys (Masuck et al., 2011) cleaning products (Nicolas et al., 2011), personal computers (Yoon et al., 2011b) and television sets (Yoon et al., 2011a). A study by Steinemann et al. (2011) tested the emissions from 25 common fragranced consumer products, including personal care products and cleaning supplies, and found an average of 17 compounds emitted per product and 133 different compounds emitted in total, 24 of which are classified in the United States as toxic or hazardous.

1.3.1 Methods for the measurement of VOCs emitted from materials

Salthammer (2009) stated that "evaluation of VOC and SVOC emission potential of individual products and materials under indoor-related conditions and over defined timescales requires the use of climate-controlled emission testing systems". An important aspect of these emission testing systems is that the product under test is isolated from other materials. Different types of enclosure used for material samples are described below. Reference methods for emissions testing are specified for product certification, whilst simpler emissions screening tests have been developed for routine industrial applications.

1.3.1.1 ISO 16000 series standards for emissions testing

The 16000 international standards series has several standards which are relevant to emissions testing.

Part 9 of this standard series employs an emission test chamber to determine the emission of VOCs from building products and furnishing (BS EN ISO 16000-9, 2006).

An emission test chamber is defined as “an enclosure with controlled operational parameters” and conditions of temperature, relative air humidity and area specific air flow rate are defined within the standard. The air in the emission test chamber is fully mixed and measurements of the VOC concentration in the air leaving the chamber are representative of the emission test chamber air concentrations. The chamber is supplied with clean air and the chamber and the parts of the sampling system coming in contact with the emitted VOCs are normally made of surface-treated (polished) stainless steel or glass. Typically emissions test chambers range in volume from 0.020 m^3 to 50 m^3 (Salthammer, 2009). 1 m^3 is a common size for a test chamber, and an example of a 1 m^3 stainless steel chamber is shown in Plate 1-1.

Plate 1-1 1 m^3 stainless steel emissions chamber (supplied by BRE Garston, 2009)

The area specific emission rates (SERs) of VOCs from the material under test are calculated from the emission test chamber air concentrations, the air flow through the emission test chamber and the surface area of the test specimen. Products for use in

Europe are tested at 23 °C and 50 %RH. Normally duplicate air samples are taken at 72 hours and 28 days after the start of the test. ISO 16000-6 is referred to for air sampling and analytical methods for the determination of VOCs, with ISO 16000-3 being referred to for sampling and analysis of formaldehyde. There is a further test method for formaldehyde specifically from wood-based panels (EN 717-1:2004) which involves a chamber test and determination of the steady state formaldehyde concentration in the air by an impinger technique based on the reaction of formaldehyde with ammonium ions and acetylacetone followed by photometric analysis.

Part 10 is a parallel standard employing an emission test cell (BS EN ISO 16000-10, 2006). The emission cell concept was developed in 1991 by a Scandinavian group of researchers. An emission test cell is a small chamber that is placed on the surface of the material under test and is designed such that the surface of the material becomes part of the cell (Wolkoff, 1996). Their objective was to address the need for a small, versatile and easy-to-use tool for both non-destructive on site (field) measurements of surface emissions and laboratory emissions tests. An example of a test cell is the Field and Laboratory Emission Cell (FLEC), shown in Plate 1-2. The cell is supplied with pure and humidified air, the air inlet of the cell being designed such that the flow of air is directed over the entire surface of the material under test before exiting the cell through a central exhaust point. The internal air volume of the FLEC is approximately 35 ml.

Plate 1-2 The Field and Laboratory Emission Cell (FLEC)

Part 11 complements parts 9 and 10 by defining the procedure for "Sampling, storage of samples and preparation of test specimens" (BS EN ISO 16000-11, 2006). There are separate specifications for solid, liquid and combined building or furnishing products.

A solid product is defined as a resilient or rigid product whose properties meet user-specifications directly without a transition phase e.g. curing or drying. Examples of resilient products are insulation products and wall coverings. Examples of rigid products are laminated flooring, wood panels and ceiling materials. A liquid product is defined as one whose properties meet the user-specifications after a transition phase, e.g. curing or drying. Examples of liquid products are paints, levelling compounds and sealants. A combined product is one which is formed on-site by the combination of more than one solid or liquid product. Examples are glued applications such as floor and wall coverings that are fixed on the site on surfaces using adhesives and penetrating oil or stain applied to wood. A combination of products can result in emissions which are different from the sum of those emitted by the components. The total amount and type of VOCs as well as the emission profile over time may be influenced by the interaction of the components. ISO 16000-11 contains a general principle for how such testing should be performed.

Further parts to the ISO 16000 series of standards also apply chamber technology. Parts 23 and 24 of the series describe performance tests for evaluating the reduction in concentrations of VOCs and formaldehyde respectively by sorptive building materials (BS ISO 16000-23, 2009; BS ISO 16000-24, 2009). The new standards have been produced to provide a means of comparative assessment of the performance of different sorptive materials marketed for removing airborne pollutants either via physical sorption or chemical reaction. Part 25 (BS ISO 16000-25, 2011) aims to provide a standard test procedure for measuring SVOC emissions from construction products. SVOCs, such as phthalate esters, are found in many construction materials and if emitted into the air they can stick to surfaces and become a persistent indoor air contaminant, posing a potential long term health risk to building occupants. This standard employs a micro-chamber such as the Markes Micro-Chamber/Thermal Extractor™ (µ-CTE™), as described in Section 1.3.1.3. It involves a two-step process in which a sample is first placed in a micro-chamber at 23 °C and 50 % RH for 24 hours, at the end of which time an air sample is taken using a sorbent tube. The test specimen is then removed and the micro-chamber is heated to around 200 °C to 220 °C, under a flow of inert gas for 40 minutes, during which time a second air sample is taken.

Part 28 (BS ISO 16000-28, 2012) addresses a related area of concern, that of sensory testing from building materials and products.

1.3.1.2 Comparison of emission chambers and emission cells

Wolkoff et al., (2005) undertook a comparison of emission cells and small chambers for materials emissions testing. This included a listing of the technical parameters of the FLEC and emissions chambers (Table 1-4). Wolkoff et al. also summarised results from 12 inter-laboratory (round robin type) studies of emissions from a range of material types. Despite their widely different parameters, correlation between data from chambers and cells was generally found to be satisfactory (i.e. within 25 % difference), especially for dry products where the dominating emission process is internal diffusion. However in the case of drying or curing products, the primary emission process is normally external diffusion, which is significantly affected by both surface air velocity and the sample loading factor, so rigorous control of parameters prior to and during testing is required to achieve reproducible results.

1.3.1.3 Screening tests for chemical emissions

Historically, methods for screening of VOC emissions have normally involved GC analysis of the volatile content of liquid applied products (Woolfenden, 2009). An example of this is the standard method for measuring the VOC content of paints (BS EN ISO 11890-2, 2006). Another screening method has been direct thermal desorption with GC/MS analysis of small solid or liquid samples. However, correlation of such VOC content data with results from reference emissions tests can be problematical. It also has limitations for the determination of emissions from laminate materials (Markes, 2010).

Table 1-4 Comparison of technical parameters for the FLEC and emissions chambers and implications for product testing (Wolkoff et al., 2005)

Parameter	FLEC	Chamber (≤1 m^3)	Impact of difference
Air change rate (h^{-1})	~200 to 600	Typically 0.5 to 1	Not significant, realistic air velocities
Air supply (l min^{-1})	0.2 to 1	0.5 to 20	> 500 l chambers more expensive to run than cells or smaller chambers
Air velocity (m s^{-1})	0.01 to 0.1	<0.1 to 0.3	Different air velocities result in different SERs for external diffusion emissions (K_g>>K_s)
Distribution of air	Constant but uneven distribution	Uneven, varies with sample orientation	For cells and the smallest chambers: multi-tests are needed for materials with point sources
Sample area	177 cm^2	Depends on loading	Cells more likely to require repeat tests on inhomogeneous materials
Loading (m^2 m^{-3})	510	0.5 to 1	Counter balances difference in exchange rate
Volume	35 cm^3	20 l to 1 m^3	No still air in cell – minimises sink effects
Equilibration time	minutes to hours	hours to days	Cells allow higher experimental throughput

K_g = gas-phase mass transfer coefficient, K_s = source phase mass transfer coefficient

A Micro-Chamber/Thermal Extractor (µ-CTE) has been developed by Markes International to allow rapid surface or bulk emissions testing of up to six samples simultaneously (Markes, 2009). The µ-CTE consists of six separate cylindrical chambers made of stainless-steel (28 cm deep and 45 mm diameter). The volume of the micro-chamber available for bulk emissions testing is about 44 cm^3 and, when testing surface emissions, 12.82 cm^2 of sample surface is exposed to the air flow and the air volume above the sample surface is 3.2 cm^3. A schematic of a µ-CTE chamber showing the positioning of samples for both surface and bulk emissions testing is given in Figure 1-1. The µ-CTE can be operated at ambient temperature or up to 120 °C. A temperature of between 30 and 65 °C is typically used for materials emissions testing. The reasoning for use of a temperature above ambient is that equilibration will be quicker and sensitivity increased, but the emission profile will not be significantly changed (Markes, 2010).

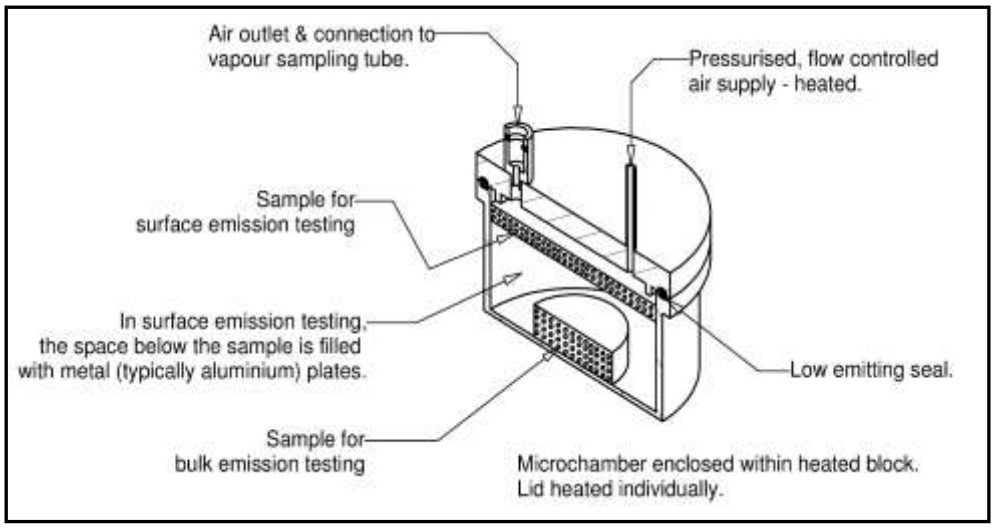

Figure 1-1 Cross-section of a µ-CTE chamber showing samples in place for surface and bulk emissions testing (supplied by Markes International, 2010)

Conditioned sorbent tubes are attached to each micro-chamber and a controlled flow of air is passed through all chambers. Air enters at the top of each unit and is directed down onto the surface of the sample contained within the micro-chamber. VOC vapours are swept from the sample material and onto the attached sorbent tube. After sample collection, trapped vapours are thermally desorbed and analysed by TD/GC/MS. A second version (the µ-CTE250) has recently been introduced which consists of four chambers each of 114 cm^3 capacity and allows heating up to 250 °C. This model can be used for SVOC emission testing according to ISO 16000-25:2011. The two µ-CTE models are shown in Plate 1-3.

The performance of the µ-CTE was investigated by testing the emissions of VOCs from the surface of a PVC wall-covering (Dwan et al., 2006). The material was also tested in a 1 m^3 glass emission chamber. Area specific emission rates were determined for up to 3 days for the µ-CTE and for day 3 for the conventional emission chamber. Good correlation was found between the two techniques, with emission rates determined from the conventional emission chamber being some 15 % higher than those obtained from the µ-CTE. The µ-CTE was also shown to provide meaningful emissions data within 20-30 minutes due to the small size of chamber and high air exchange rate through it (typically 1000-2000 h^{-1}) which results in negligible time being required for equilibrium to be established.

Plate 1-3 Markes Micro-Chamber/Thermal Extractor, standard and high temperature models (supplied by Markes International, 2010)

Schripp et al., (2007) investigated the performance of the µ-CTE further. Three types of materials were tested, granular acrylonitrile butadiene styrene, a material used in the automotive industry and in computer monitors, polyurethane (PU) foams used in insulation and as seat padding material, and two PVC wall coverings. For all the samples studied, good qualitative correlation was found between the µ-CTE and a 1 m^3 chamber. Quantitatively the µ-CTE gave greater recovery of semi-volatiles such as 2,4,6-di-tert-butylphenol (butylated hydroxytoluene, BHT). This enhanced sensitivity for SVOCs in micro-chambers relative to conventional chambers has been observed previously (Uhde and Salthammer, 2006), being a result of reduced sink effects. For the PU foam, reproducible results were obtained for the three most important VOCs emitted. For both of the wall-coverings, good quantitative correlation was obtained in the area specific emission rates of 2-ethylhexanoic acid (2-EHA) at 3 days between the two methods. The 3-day tests indicated that the amount of 2-EHA released from the two materials differed by a factor of four. This ratio of emissions was also observed when the µ-CTE was used to test freshly unpacked material. The authors concluded that these results suggest that the µ-CTE can usefully be applied to screening of emissions from materials directly from the production line.

A major study involving comparison of emissions chambers and screening tests was the "Horizontal Evaluation Method for the Implementation of the Construction Products Directive (HEMICPD)" (Lor et al., 2010a). This was prepared by a group of Belgian

researchers and involved emissions tests on a range of building materials using a large (50 m^3) chamber, a 1 m^3 chamber, a FLEC and a µ-CTE with all tests being conducted at 23 °C. Qualitative comparison using principal component analysis of data from four floor covering materials tested after 3, 7 and 28 days showed that each chamber generated the same chemical profile for the same material.

An initial semi-quantitative comparison between techniques used in the above study showed a satisfactory (<25 %) difference in area specific emission rates obtained using the 1 m^3 chamber and the FLEC, whilst higher results were obtained using the µ-CTE. Two modifications to the procedure were made in an attempt to improve this correlation, namely that the materials were kept in the µ-CTE for the whole 28 day period and the flow rate through the chambers was reduced from 100 to 25 ml min^{-1} (in order to have a closer area specific air flow rate to that used in the other methods). Good agreement was obtained between the FLEC and µ-CTE for a PVC (polyvinylchloride) flooring and a carpet, whilst for a linoleum good agreement (<20 % relative standard deviation) was found for eight studied VOCs and a higher value for four other compounds. They suggested that this could be due to inhomogeneity in the material. Finally an insulating material (XPS with a wood wool backing) was tested. This material was found not to give an air-tight seal with the FLEC. Results obtained from parallel measurements were made with and without a sub-unit that contained the sample and enabled an airtight seal with the FLEC and these gave different results. This showed the importance of taking into account the porosity of the material. Some variations in results were also found between three replicate µ-CTE measurements for this material. Correlations between average TVOC values for the µ-CTE and the FLEC (with sub-unit) after 3 and 7 days were good, but greater divergence was found after 28 days. The emission rates of two individual chemicals, n-pentane and styrene, showed significant differences between the two techniques, however, for both compounds the emissions profiles using the µ-CTE and the FLEC behaved the same over time. They concluded that the µ-CTE is a suitable tool for the screening of building materials (Lor et al., 2010a).

Abba et al. (2011) investigated the emissions of three water based paints with different formulations using a 100 litre chamber (according to ISO 16000-9:2006) and the µ-CTE

(set at 40 °C) with air samples being taken after 18 and 24 hours. They also undertook testing of VOC content of the paints using an 'in-can' method (BS EN ISO 11890-2, 2006). One of the paints contained a coalescing solvent with a boiling point >250 °C (the cut-off point for the VOC content method). They found that the in-can method was not sufficient to describe the effect on IAQ. They concluded that complementary emission testing is necessary and that, in conjunction with a traditional longer term chamber test, the µ-CTE is helpful for pre-screening of emissions. Kang et al., (2012) have used the µ-CTE to provide a fast screening method to determine the emission of one particular compound of concern (naphthalene) from a series of building and furnishing materials and consumer products. A further report described a study of VOCs and SVOCs from desk mats and artificial leathers using the high-temperature version of the µ-CTE (Jinno et al., 2011). This study used a method similar to that described in the new standard for measuring SVOCs from building products (ISO 16000-25:2011).

Therefore the µ-CTE provides a complementary approach to that of emission chambers which require significant equilibration times. Qualitative and semi-quantitative screening of product emissions after minutes of equilibration rather than hours/days may provide a quick screening tool for quality control of production and other in-house tests by manufacturers. The possibility of using a higher temperature for the test can increase the sensitivity of the technique and may also represent a worst real case for some material exposure as might be caused, for example, by sunshine on indoor surfaces.

1.3.1.4 Other international standards for emissions testing

A further series of standards have been produced by CEN specifically to determine emissions from adhesives after their application (EN 13999-1 to EN 13999-4). The standards apply to 'solvent-free' and 'low-solvent' adhesives which are applied at room temperature. The first part is a general procedure; the second part describes the determination of VOCs, the third part the determination of volatile aldehydes and the fourth part the determination of volatile diisocyanates. The test is performed in an emission test chamber at specified conditions and a stainless steel or glass plate is used as a substrate onto which the adhesive is applied. Sampling and analysis for VOCs is undertaken at specified times after the prepared test specimen is placed in the centre of

the chamber (with determination of carcinogenic and sensitizing substances after 24 hours). The methods used for sampling and analysis of VOCs and aldehydes are based on those in ISO 16000-6 and ISO 16000-3 respectively, while that for diisocyanates is based on chemisorption with 1-(2-methoxyphenol) piperazine impregnated filters followed by desorption and liquid chromatographic analysis with UV detection.

Also of interest with respect to emissions from materials is a series of standards concerned with air pollutants inside road vehicles which have been published during the course of the project. Part 1, which is a "Specification and method for the determination of volatile organic compounds in car interiors", employs a test chamber which can accommodate a whole vehicle (BS ISO 12219-1, 2012). Part 2, which is a "Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials", involves placing one or multiple test samples in a sampling bag and heating at a specified temperature after which the gas in the sampling bag is collected to measure the test concentrations (BS ISO 12219-2, 2012). Part 3 is titled "Screening of chemical emissions from car interior trim components - Micro-scale chamber method" and employs the µ-CTE (and other similar products) for rapid screening of emissions (BS ISO 12219-3, 2012). There are further parts of this standard series under development which specify other chamber types, measurement of SVOCs and odour determination (ISO, 2013). Micro-scale chambers, including the µ-CTE, are also specified in the ASTM (American Society for Testing and Materials) method D7706-11 entitled "Standard practice for rapid screening of VOC emissions from products using micro-scale chambers" (ASTM, 2011).

Another relevant international standard is BS ISO 10580:2010, which describes a test method for emissions of VOCs from resilient, textile and laminate floor coverings. This standard was based on a draft European standard (prEN 15052, 2004) for the evaluation of VOC emissions from these materials. The emissions test chamber system is based on ISO 16000-9 and sampling and analysis of VOCs on ISO 16000-6. Following analysis, evaluation is undertaken either using a procedure which is applicable within Europe or one relevant for North America. The European procedure involves measuring concentrations of total VOCs and of carcinogenic compounds, emitting from the floor

covering after 3 days and 28 days. After 28 days additionally, using a list of assessable compounds, a risk factor is calculated by summing the ratios of the concentration of each compound and the "lowest concentration above which, according to best professional judgement, the compound might have an adverse effect on humans in an indoor environment" (BS ISO 10580, 2010). This 'lowest concentration of interest' concept is also made use of in the German AgBB scheme (see Section 1.3.3.1).

1.3.2 Typical organic compounds released from various materials

Numerous investigations of emissions of VOCs from construction and consumer products have been undertaken by research groups across the world. Some studies have just looked for the presence of particular compounds, perhaps because of concern over their toxicity or irritancy, while others have investigated a wider range of compounds. It is difficult to establish a comprehensive list of which VOCs are emitted from which sources because of the on-going variation in the production of products and the resulting change in the composition of the mixture of VOCs emitted, however some examples of particular compounds emitted from a selection of materials are given in Table 1-5, together with some details of the method used to undertake the test.

Table 1-5 Examples of chemicals emitted from selected materials and products

Material(s) tested	Chemical(s) emitted	Details of test	Reference
PVC flooring	Phthalates	50 l chamber and FLEC Tenax, TD/GC/MS	Afshari et al., 2004
Wall coverings	Phthalates	1 m^3 glass chamber Tenax, TD/GC/MS	Uhde et al., 2001
Latex paints	Formaldehyde	0.05 m^3 steel chamber DNPH/HPLC/UV	Chang et al., 2002
Latex paints	Texanol ester alcohol	3.3 l Stainless steel chamber, Tenax, TD/GC/FID	Lin and Corsi, 2007
Linseed oil paints	Aldehydes	Emissions chamber and LC/MS analysis	Fjallstrom et al., 2003
Various consumer products	p-Dichlorobenzene	'Walk-in' chamber, Tenax, TD/GC/FID	Guerro and Corsi, 2009
Polyurethane foam	Flame retardants	1m^3 glass chamber Tenax, TD/GC/MS	Salthammer et al., 2003
Polyurethane adhesives	Isocyanates	2.2 l and 1 m^3 chambers HPLC/UV/MS	Wirts et al., 2003
Cleaning products and air fresheners	Glycol ethers and terpenoids	50 m^3 room Tenax, TD/GC/MS	Singer et al., 2006
Oriented Strand Boards	Range of VOCs	FLEC, Tenax, TD/GC/MS DNPH/HPLC	Däumling et al., 2009
Gypsum based materials	Sulfur containing compounds	4l-headspace vessels Tenax, TD/GC/FID/MS	Burdack-Freitag et al., 2008
Pinewood furniture boards	Range of terpenes	1m^3 glass chamber Tenax, TD/GC/MS	Uhde and Schulz, 2008
Cork products	Phenol and furfural	1m^3 glass chamber Tenax, TD/GC/MS, DNPH/ HPLC	Horn et al., 1998
MDF overlaid with various materials	Formaldehyde and a range of VOCs	FLEC and 20 l chamber, Tenax, TD/GC/MS, DNPH/HPLC	Kim et al., 2010
10 exotic wood products	Range of VOCS and aldehydes	225 l Stainless Steel chamber, Tenax, TD/GC/MS, DNPH/ HPLC	Kirkeskov et al., 2009
Vinyl ester resin thermoset composite	Styrene	Solvent desorption, GC-FID	Crawford and Lungu, 2011

1.3.3 Labelling schemes for material emissions

1.3.3.1 Europe

In response to the need for improved consumer protection, a number of low VOC emission labels for construction products have been developed in Europe over the last twenty years, some having arisen from government initiatives and others being industry based (ECA, 2005). The focus of most of these labels is the classification of emissions into indoor air, sometimes this is combined with restrictions of some ingredients in the product. Most of the labels are used on a voluntary basis, but in a number of cases mandatory requirements have either been established or are planned. Some large companies, such as the automotive industry and IKEA, have also established their own specifications of low VOC emissions that their suppliers have to fulfil. A number of the labelling schemes in existence throughout Europe are described below:

Finnish M1 scheme – this is a voluntary classification scheme which includes "target values for indoor air quality and climate, cleanliness requirements for construction works and emissions criteria for all types of building materials" (Sateri and Sariola, 2009). The scheme was first applied in Finland in 1995. The classification was updated in 2001 and again in 2008. Materials which pass the emission criteria are given an M1 label. In February 2009 there were over 1,300 M1-labelled building products from over 130 companies and 14 countries around the world.

Danish Indoor Climate Label (**DICL**) – this is a voluntary scheme which is applicable to all product types with relevance to indoor air (Witterseh, 2009). It was proposed by the Danish Ministry of Housing and Urban Affairs in 1993 in order to reduce emissions from materials used indoors. Specific criteria have been developed for a number of product areas including 'textile floor coverings' and 'windows and exterior doors'. Products are tested for emissions on a minimum of two occasions, and concentrations of individual compounds are compared against threshold values for irritation of mucous membranes. This labelling scheme also includes sensory testing.

"Ausschuss zur gesundheitlichen Bewertung von Bauprodukten [Committee for Health-related Evaluation of Building Products]" (**AgBB**) scheme – The first version of the AgBB scheme was published by the German government in 2001 (Däumling, 2009). Since 2004 the scheme has been included in the approval procedure for some

construction materials in Germany by the Deutsches Institut fur Bautechnik [German Institute for Construction Technology] (DIBt), so in this context it is a mandatory scheme (Kirchner et al., 2009) and was notified to the European Commission in 2005. Kirchner et al. reported that by 2009 the mandatory scheme had been applied to floor coverings and related adhesives and that, since 2005, DIBt had granted 234 technical approvals (covering more than 1000 products due to group approvals) for floor coverings tested and evaluated. The scheme also applies on a voluntary basis with the aim of fostering the development of a wide range of low emission building products.

The evaluation includes limits for the total amount of emissions, assessment of the toxicological significance of individual compounds detected and limits for non-assessable substances. The scheme covers both VOCs (n-hexane, nC_6, to n-hexadecane, nC_{16}) and SVOCs ($>C_{16}$ to C_{22}). The basis for the evaluation of individual compounds is "a list of 'Lowest Concentration of Interest' (LCI) values which are updated periodically based on actual toxicological knowledge" (Däumling, 2009). There are also particular requirements for carcinogenic compounds. Updates to the scheme, containing new and revised LCI values, are published at intervals of about two years. At the start of the present project the version of the evaluation procedure published in 2008 was current. This listed LCI values for 164 compounds and also included in the list 11 VVOCs without LCI values. An updated list was published in May 2010, which included seven new compounds, revisions to the LCI values of a number of the compounds and removal of the LCI value for tributyl phosphate (which is classified as an SVOC). A further update was published in June 2012 (AgBB, 2012) which included seven new compounds and a number of revisions to LCI values. One compound (tetrachloroethene) was removed from the list, so that currently 176 compounds have published LCI values. It states in the evaluation procedure that VVOCs "are not currently considered in the AgBB evaluation", however a paper reviewing 10 years of the AgBB scheme (Däumling, 2012) reports that inclusion of these compounds is planned as part of the next stage of AgBB development.

"L'agence francaise de securite sanitaire de l'environment et du travail [French Agency for Environmental and Occupational Health and Safety]" (**AFSSET**) scheme – A working group established by AFSSET and co-chaired by Centre Scientifique et

Technique du Batiment [French Scientific and Technical Centre for Construction] (CSTB) started its work in 2004 (Maupetit and Mandin, 2009). A voluntary protocol for the evaluation of VOC emissions from solid building products was produced in 2006. The evaluation is based on a similar approach to that of the AgBB scheme. The latest version of the AFSSET scheme, which has now been extended to liquid products, was published in 2009 and lists LCI values for 165 compounds (AFSSET, 2009). (Note that AFSSET has been replaced by ANSES, the French Agency for Food, Environmental and Occupational Health and Safety). While many of the compounds listed in the AFSSET scheme are the same as those in the AgBB scheme, some of the LCI values differ widely between the two schemes.

The scheme has not been endorsed by voluntary labelling schemes in France and promotion of low emitting products has remained extremely limited (Maupetit and Mandin, 2009), so the French government is undertaking mandatory labelling of VOC emissions from building and decoration products. This decision is part of the consensus action called 'Le Grenelle Environement' which also defines energy saving objectives for the building sector. The French government notified the European Commission of this intention in 2010 (European Commission, 2010) and a decree was issued on 23rd March 2011 stating that products may only be made available on the market if they are accompanied by a label, applied to the product or its packaging, indicating their emissions of VOCs. TVOCs and 11 individual compounds from the AFSSET protocol were listed on the draft order. Butyl acetate was later removed from the list and the 10 remaining compounds have to be assigned to one of four emission classes. There is also a separate list of four CMR[1] compounds category 1 and 2 (since categorised as 1A and 1B) which need to be kept at very low concentrations. The provisions of this decree came into force on 1st January 2012 (Ministère de l'Ècologie, du Devéloppement Durable, des Transports et du logement, 2011) for new products and apply to existing products from September 2013 (Maupetit, 2011).

A new draft **Belgian** regulation, notification number 2012/568/B, on VOC emissions from a number of construction product types was notified to the European Commission

[1] Carcinogenic, mutagenic or reprotoxic

in October 2012 (Kingdom of Belgium Federal Public Service of Health, Food Chain Safety and Environment, 2012). This is expected to be published during 2013. The regulation intends to define maximum emission of VOCs, the limits are similar to the German regulation, but with some differences in the details. Compliance will be by self-declaration and there will be no labelling requirements.

GUT label – this was established in Germany in 1990 by Gemeinschaft umweltfreundlicher Teppichboden (GUT) e.V. as a voluntary labelling system to show the low VOC emission performance of textile floor coverings (Vankann, 2009). Since 2007 the scheme has been extended into a full product information system (PRODIS) that additionally informs about the use and life cycle aspects of the tested carpets. Carpet producers from all over Europe participate in GUT's environmental programme, covering more than 85 % of the EU production volume for textile floor coverings. Compliance with GUT's criteria is achieved by three stages of product testing: an odour test, a pollutant test for hazardous non-VOC substances and an emissions test. The evaluation of monitored emissions uses similar criteria to those of the AgBB scheme.

EMICODE – This system was established in 1997 as a voluntary scheme promoted by the German adhesives manufacturers association to define a low VOC emitting adhesive (Winkels, 2009). Products are tested for release of carcinogenic substances after 1 day in a test chamber, then for total VOCs after 10 days. The EMICODE label can be applied to primers, levelling compounds, adhesives, underlays and joint sealants. Most flooring adhesives used in Germany are now EMICODE labelled and its use also extends to several other European countries.

The Blue Angel – The Blue Angel is a voluntary eco-label set up by the German government in 1977 (Plehn and Horn, 2009). From 1986 the scheme was broadened to include chamber testing for a range of product types. Wood based products were the first items to have criteria established. Initially only formaldehyde concentrations were limited, with VOC emissions being included in 1998. The scheme has since been extended to cover a wide range of materials and products used indoors. The criteria are similar to those for the AgBB scheme, but stricter, the Blue Angel aiming to award products which have especially low emissions.

In the UK, while the benefits of low emitting products are recognised in the guidance contained in Approved Document F supporting ventilation requirements in the building regulations (HM Government, 2010), there are no national labelling schemes and the government's Code for Sustainable Homes does not include any requirements for IAQ (HealthyAir, 2010b). However, the trend towards construction of more airtight buildings, with the possibility of inadequate ventilation, has raised concerns about IAQ, and the use of low emitting products has been recognised as one tool to prevent poor IAQ and the associated possible adverse effects on human health (Crump et al., 2009; Watson, 2008).

1.3.3.2 United States

In the United States there is a growing demand for products with low emissions of VOCs to satisfy green building rating systems (Hodgson et al., 2011). An example of these is LEED (Leadership in Energy and Environmental Design), which is administered by the Green Building Council (USA) the latest version of which specifies VOC emissions testing (Däumling, 2012). Levin, reviewing the material emission and certification programs existing in the USA in 2010, stated that these "began as a response to increased complaints of health effects associated with reduced ventilation intended to conserve energy in the 1970s". Since this time a number of standard methods and certification schemes have been developed independently by a range of organisations. Some of the more important of these are described below:

California Standard Practice Section 01350 – 'Cal01350' was developed by the California Department of Public Health (CDPH) in 2000 to define a VOC emission testing protocol and emission limits. The first edition of the "*Standard Practice for the Testing of Volatile Organic Emissions from Various Sources Using Small-Scale Environmental Chambers (Standard Practice)"* was produced in 2004 (Stensland, 2009). The aim was improved information for the selection of interior building materials. The testing protocol was linked to the state's exposure guidelines, known as Chronic Reference Exposure Levels or CRELs, and includes probable or known carcinogens, reproductive/ developmental toxins and systemic toxins with non-cancer chronic effects. Stensland (2009) also states that testing is undertaken according to ASTM (American Society for Testing and Materials) D5116-05 "Standard Guide for

Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products". The Standard Practice/Cal01350 is used for a variety of dry product groups including carpets, wood, resilient flooring and wall coverings. An updated edition of this standard method was produced in February 2010. This stated that "VOCs emitted by products appearing on State of California lists of toxic substances are considered to be chemicals of concern" are required to "be included as target VOCs for the testing of emissions under this method" (CDPH, 2010). As well as the CREL list the standard method includes website addresses linking to the latest published editions of two other lists which contain the relevant chemicals.

Californian Collaborative for High Performance Schools (**CHPS**) – the CHPS requires that contractors bidding to construct new schools and other public building projects guarantee only to use materials whose emissions have been tested using the Cal01350 protocol by an accredited laboratory (Woolfenden, 2009).

The ANSI/BIFMA Furniture Emissions Standards – The BIFMA Furniture Emissions Standards were established in 2005 by the Business and Institutional Furniture Manufacturers Association International (BIFMA) following ten years of development by a broad group of stakeholders (Carter, 2009). The American National Standards Institute (ANSI) approved the standards in 2007 as American National Standards for determining low-emitting VOC performance for business and institutional furniture products in North America and any other interested country. ANSI/BIFMA M7.1 is a consensus based test method for determination of individual and total VOC emissions, including aldehydes, from furniture under environmental and product usage conditions that are representative of those in office buildings. ANSI/BIFMA X7.1 is a consensus based conformance standard for low-emitting furniture that specifies acceptance levels for the emissions of VOCs, including aldehydes from newly constructed office furniture systems and seating when tested per ANSI/BIFMA M7.1. The standards were revised in May 2011 with changes to some emissions factor criteria (GEI, 2010b).

The Green Label Plus program – The Green Label program was launched in 1992 by the Carpet and Rug Institute (CRI) to help specifiers to identify products with very low emissions of VOCs. The latest revision, renamed Green Label Plus (GLP), includes

carpets and adhesives (Hurd, 2009). CRI is an ANSI accredited product certifying body. To receive initial certification, products are tested after 14 days as required by Cal01350. The product is further tested on a quarterly basis against established emissions criteria for TVOCs, then on an annual basis for TVOCs plus levels of 13 chemicals (for carpets) and levels of 15 chemicals (for adhesives).

FloorScore Flooring Products Certification program – FloorScore is a voluntary, independent certification program which was established in 2005 by the Resilient Floor Covering Institute in conjunction with Scientific Certification Systems (SCS). SCS acts as a third-party certifier ensuring program integrity and independence. FloorScore tests and certifies hard surface flooring for compliance with Cal01350 criteria using a small-scale chamber test protocol. It encompasses a wide range of flooring products, for example linoleum, laminate flooring and ceramic flooring and associated products (Freeman, 2009). By 2009, 15 hard surface flooring manufacturers from North America, Europe and Asia had certified over 300 flooring products in the FloorScore program.

Greenguard Certification Program – the Greenguard Certification Programs are developed by the Greenguard Environmental Institute (GEI) which was established in 2001 as an industry-independent, not-for profit organization with the aim of "protecting human health and quality of life through programs that reduce chemical exposure and improve indoor air quality" (GEI, 2010a). This website states that the institute currently runs three product certification programs: 'Greenguard Indoor Air Quality Certified' which applies to "low-emitting building materials, furniture, furnishings, finishes, cleaning products, electronics and consumer products", 'Greenguard Children and Schools Certified' for "products used in environments where children and other sensitive populations spend extended periods of time" and 'Greenguard Premier Certified' which is "a comprehensive health-based certification program for which products of all types are eligible". The GEI provides a range of product standards that are required to be met for Greenguard certification. Their primary test method used for most building materials, furniture and finishes is the "Standard Method for Measuring and Evaluating Chemical Emissions from Building Materials, Finishes and Furnishings using Dynamic Environmental Chambers" (GEI, 2011).

1.3.3.3 Other countries

A number of other countries worldwide are developing labelling schemes for emissions from materials. Examples of these include Japan and Korea. Azuma et al., (2008) reviewed the governmental and industrial standards and guidelines concerning labelling of emissions in Japan. They reported that several labelling systems exist, for example the wallpaper industry has established voluntary standards for emissions of VOCs from their products based on the German labelling systems. Levin (2010) reported that mandatory testing is required under the Building Standards Law, while voluntary certification of some materials is undertaken by the JIS (Japanese Industrial Standards) product certification system. The Japanese standard for emission of VOCs covers the following building products: building boards, wallpaper and flooring materials, adhesives, paints and coating materials and heat insulating material boards.

Likewise Korea has established testing programs and limits on emissions, but there is no central authority for IAQ or emissions testing, certification and labelling. The Korean National Institute of Environmental Research tested nearly 1,500 construction materials over the period 2004/2006 and as a result "issued a notice of restriction on the use of 145 materials exceeding the standards" (Levin, 2010). On-going work by the Korean government and research institutions is developing policies and regulations regarding emissions (Kim and Lee, 2011).

1.3.4 Summary of analytical requirements for labelling schemes for materials emissions

A review of labelling schemes and product testing programs was included in a 'state of the art' report prepared as part of the HEMICPD project (Lor et al., 2010b). They reported that the programs evaluate the test results obtained in three different manners, either by just restricting the total emissions of VOCs, the so-called TVOC value, by limiting all VOCs with low irritation thresholds and odour thresholds, or by setting limit values for a longer list of chemicals depending on their specific toxicological properties. They noted that the last of these approaches, involving so-called LCI (Lowest concentration of interest) values, was being increasingly applied. Most of the labelling schemes were found to use similar measurement methods, though the results are often

evaluated differently and include differences in the VOCs measured, limit values and measurement conditions. In particular they observed differences in the TVOC calculation procedure in labelling schemes which use this concept (Lor et al., 2010b).

Table 1-6 summarises the main analytical requirements of the four national labelling schemes within Europe. The test procedure and the analytical methods in the schemes are all based on those described in ISO 16000 standards parts 3, 6, 9, 10 and 11, but differences exist in the detail of the requirements for each scheme.

Table 1-6 Comparison of analytical requirements for European labelling schemes (ECA, 2012)

Requirement	M1	DICL	AgBB	AFSSET
Measuring points (days)	28	3, 10 and 28	3 and 28	3 and 28
Formaldehyde measured	Yes	Yes	No	Yes
TVOC measured	Yes	No	Yes	Yes
SVOC measured	No	No	Yes	No
Single VOCs measured	Some	Yes	Yes	Yes
Evaluation of carcinogens according to	IARC [1] Class 1	IARC Class 1	EU Class 1A and 1B	EU Class 1A and 1B
Irritants evaluated	Ammonia	Selected VOCs	All VOC according to LCI values	All VOC according to LCI values
Other VOCs assessed	No	No	Yes	Yes

[1] IARC = International Agency for Research on Cancer

1.3.5 Harmonisation of labelling schemes and standards for emissions testing within Europe

The proliferation of labelling schemes for low emitting construction products across Europe is a financial burden for manufacturers who wish to sell such products throughout the continent. In response to this concern the European Commission's Joint Research Centre (JRC), Ispra, Italy has encouraged activities to investigate the scope for harmonisation of these existing schemes (Kephalopoulos et al., 2009). It was felt that

there was a need for common testing and analytical procedures, with the possibility of labelling in accordance with different schemes being achieved from one emission test (and that this could be achieved in advance of full harmonisation). The initiative was taken forward by a conference in Berlin in June 2007, organised in the context of the German EU presidency, entitled "Construction Products and Indoor Air Quality" (Ahrens et al., 2007) and the formation of a working group with representatives of the Danish (DICL) and Finnish (M1) labelling schemes and the German AgBB scheme, as well as participants from emission test laboratories in the UK, France and the JRC. The working group has produced a report on common requirements of a harmonised scheme. This was informed by round robin testing of products according to the individual schemes and comparison of the results obtained (ECA, 2012).

There is also on-going work within the European Standards Organisation (CEN) to prepare harmonised test protocols to determine the emission of dangerous substances from construction products in support of the Construction Products Directive (CPD) (European Commission, 1989). The CPD is "European legislation that was developed with the objective of ensuring free circulation and use of construction products in the Internal Market of the European Union" (HealthyAir, 2010a). One of the six Essential Requirements (No. 3: Hygiene, Health and the Environment) requires that construction work be designed and built in such a way that it will not be a threat to the health of occupants (Woolfenden, 2009). The CPD is being replaced by the Construction Products Regulation (CPR); text for the CPR was agreed and the European Parliament voted in its favour on 18th January 2011 (European Parliament, 2011). The regulation (305/2011/EU) was adopted on 9th March 2011 (European Commission, 2011). The main parts of the CPR apply from 1st July 2013.

To prepare for the coming into force of the CPR, CEN established a new technical committee (TC351) in 2007 to develop standards concerning the release to soil, air and water of regulated dangerous substances (HealthyAir, 2010a). A working group specific to indoor air has drafted a new European standard (EN). Emissions data produced by applying the proposed EN is intended to be used for CE marking of construction products and attestation of conformity. The new standard is based on the ISO 16000 series of standards and is applicable to VOCs, SVOCs, volatile aldehydes and volatile

diisocyanates. The rates of release of dangerous substances from new products are to be measured at specified times after the product is placed in a test chamber. The test conditions have been chosen to enable the "results to be converted to a concentration in a reference (or typical) room by calculation" (HealthyAir, 2010a). This reference room, together with the testing duration, defines an exposure scenario by setting room dimensions, the rate of air exchange, the temperature and humidity and the surface area of particular product types present in the room. Measurements after 3 days are to assess short term emissions from new products and those after 28 days are to assess potential long term exposure. The new standard was first issued as a draft technical specification (Draft TS 00351006 - Assessment of emissions of regulated dangerous substances from construction products – Determination of emissions into indoor air) and it has since been approved by CEN TC351. The technical specification is expected to be published as CEN/TS 16516 during the summer of 2013 with transformation into a full EN norm in 2015.

Robustness testing of the draft test method for determining VOC emissions using different conditions such as loading and air exchange rate has been undertaken (Wilke et al., 2012). In common with existing schemes in Germany and France, it is proposed to incorporate LCI values for target chemicals in the product assessment process. The working group established by the JRC is developing a procedure for deriving harmonised LCI values (JRC, 2011). These values, along with criteria for TVOC concentrations, carcinogenic substances and the amount of non-assessed compounds (i.e. those without an LCI value) are expected to form the basis of assessment of products for regulatory and voluntary schemes using emission chamber methods with VOC measurements after 3 and 28 days of test.

A number of 'indirect' methods are also referred to in the forthcoming EN. Such methods are deemed to be acceptable "provided their comparability or correlation to the reference chamber method has been demonstrated in their specific field of application" (HealthyAir, 2010a). Such methods may be easier to apply and/or cheaper and may be particularly useful for factory production control. An example of such a method is the rapid determination of the emissions from a product, perhaps at elevated temperature, using equipment such as the µ-CTE.

1.4 Reliability of emissions tests

As the results of emissions tests are used to predict the potential effects of the use of a product in an indoor environment and more specifically to determine the eligibility or otherwise of a product to receive a particular label, it is important that the results of these tests are reliable. There are numerous sources of uncertainty in the measurement of VOCs from building materials and products. These include the selection, packaging, transport and storage of the material samples, the operation of the emissions test chamber and the sampling and analysis of the emissions (Howard-Reed et al., 2008).

Confidence in results of emissions tests can be achieved through validation of the procedure used, together with on-going performance checks. An important part of method validation involves participation of analytical laboratories in external activities designed to improve performance. These can involve analysis of pre-loaded sorbent tubes. Tubes may either be supplied where the analyst is informed of analyte loading levels, in which case they are known as calibrated reference standards, or else where the levels are concealed, as is the case with a proficiency testing (PT) scheme and other inter-laboratory comparison exercises. Inter-laboratory comparisons may also test the sampling step of an emissions test. Wilke et al. (2009) suggested that an alternative means of validation of both sampling and analytical steps of an emissions test would be to employ a reference material with known emission rates of target substances which could be placed inside the test chamber.

The use of a ‘check standard’ mixture which has been suggested to improve the reliability of material emission testing, a number of recent inter-laboratory comparison exercises, the development of a PT scheme and of a reference material are described in the following sections.

1.4.1 Check standard mixture

One challenge in the analysis of emissions from materials is in the maintenance of up to date calibrations for all of the compounds contained on extensive lists of target analytes. ISO 16000-6:2011, for example, recommends that calibration standard mixtures of different concentrations are analysed with each set of samples as a check on system

performance. This gave rise to the suggestion (Woolfenden, 2009) that use of a 'check standard' mixture, containing a small number of compounds which are representative of the range of compounds of interest, would improve the reliability of analytical data produced. 11 compounds were included in this check standard mixture following discussion between personnel from several European laboratories involved in materials emissions analyses. The compounds selected were n-hexane, 4-methylpentan-2-one [methyl isobutyl ketone] (MIBK), toluene, hexanal, butyl acetate, cyclohexanone, 1,2,3-trimethylbenzene (123-TMB), phenol, butylated hydroxytoluene (BHT), 4-phenylcyclohexene (4-PCH) and n-hexadecane. The inclusion of compounds with some polarity, particularly hexanal and phenol, will provide a stringent test of the condition of the analytical system as these offer a challenge for analysis using the column type specified in ISO 16000-6:2011 and are therefore likely to be the first compounds to show deterioration in their performance.

1.4.2 Inter-laboratory comparison exercises

Oppl (2008) reviewed the results of a number of round robin tests and other comparative investigations undertaken to investigate the variability of emissions testing. The round robin tests typically involved between 10 and 20 laboratories from all over Europe which each received samples from the same test specimen on which they would perform a complete emissions test. Results of the tests were collected and compared at a central laboratory. When using materials with homogeneous emission properties several tests showed a repeatability of the procedure within one laboratory of ±20 % and variability in results from different laboratories of ±50 %. In most round robin tests the differences were found to be due to the analytical procedures. Issues involved in analysis included achieving an adequate separation of chromatographic signals to allow correct identification of peaks, the application of appropriate calibration factors and the difficulty of establishing the border between signal peaks and the baseline in a complex chromatogram.

In 2008 an inter-laboratory comparison of VOC emissions was organised by the German Federal Institute for Materials Research and Testing (BAM) on behalf of DIBt with the purpose of determining the influence of various method parameters used for test chamber measurement across different test laboratories (Wilke et al., 2009). Three

consecutive steps were undertaken by 29 laboratories from throughout Europe to investigate the influence of the analysis, the sampling and the test chamber. The first step involved the analysis of four solutions each containing the same range of analytes but at different concentrations, in the second step VOCs were determined in test chamber air and in the final step a complete emission test chamber measurement of a sealant material was carried out by the participants. Results for step 1 showed standard deviations between 8 % and 34 %. The higher standard deviations were found for the solution with the lowest concentrations and for the more polar compounds investigated. For step 2 the standard deviations of individual substances ranged between 11 % and 23 %. For step 3, standard deviations of less than 20 % were obtained for key substances, with the exception of ethanediol which exhibited a standard deviation of 39 %, thought to be due to its polarity. Other substances with high standard deviations were those occurring at very small concentrations. Results obtained therefore showed an improvement compared to earlier inter-laboratory comparisons, prompting the conclusion that the emission test chamber method is, in principle, suitable to perform an assessment of the emissions from building products. A further finding of the comparison was that use of a moderately polar GC column, rather than a non-polar column as specified in ISO 16000-6, provides advantages for the separation and quantification of polar substances, such as glycol compounds, that are becoming more common in building products.

A further inter-laboratory comparison exercise involved checking the performance of test chamber measurements for VOCs from a water based lacquer over four steps. The first two steps checked the analytical method, the third involved sampling from one chamber and for the final step emission tests were undertaken by each participating laboratory (Wilke et al., 2011a; Horn et al., 2011). 37 laboratories from nine countries took part. Variability in the results increased from step 1 to step 4 and for more polar compounds. Acceptable results were achieved in the final step for 29 of the laboratories, whilst, of the laboratories which had taken part in all four steps, only 5 % had unacceptable results.

Yrieix et al., (2010) reported results of an inter-laboratory comparison, including both emissions of VOCs (according to ISO 16000-6) and aldehydes (according to ISO

16000-3) from a panel of particleboard glued with urea formaldehyde adhesive. Six European laboratories undertook an emission chamber test according to ISO 16000-9. Results showed higher variability in the VOC emissions than in formaldehyde emissions, which was thought to be due to the natural wood components in the tested product having higher heterogeneity than that of the urea formaldehyde resin. They concluded that results from the study were consistent with those from the study organised by BAM and that "an uncertainty of around 20 % can be expected on emissions from homogeneous products and for most compounds emitted at concentrations above 10-20 µg m^{-3}. Emissions from heterogeneous products and where concentration levels are low can result in higher uncertainties (around 40 %)". A follow-on exercise tested formaldehyde emissions from plywood (Yrieix and Maupetit, 2011). Eight European laboratories undertook tests of two panels with very different emission rates. Results showed good reproducibility between laboratories and that high sensitivity was achievable by the DNPH/HPLC method.

1.4.3 Proficiency testing

Proficiency testing has the primary purpose of enabling participants to be confident about the performance of their analytical method. Unexpected inaccuracies in routine results would result in an investigation with remedial action being taken as necessary (Thompson and Lowthian, 2011). The UK Health and Safety Laboratory (HSL) has set up a material emission proficiency testing (PT) scheme based on the check standard mixture (HSL, 2011). The scheme is run under the auspices of WASP (Workplace Analysis Scheme for Proficiency) which was established in 1988 to assess the performance of analytical laboratories undertaking analysis of air samples. Sorbent tubes (Tenax TA) are exposed to a standard atmosphere of VOCs generated using controlled conditions. Up to 30 tubes are loaded simultaneously for distribution to laboratories participating in the scheme. A trial round of the scheme was undertaken with the aim of assessing HSL's loading rig for producing PT samples for this scheme and to assist in the setting of an initial standard deviation to use as a basis of performance assessment in subsequent rounds of the scheme (Butler et al., 2012). Successful results were obtained and the scheme commenced during 2012 with participant laboratories being supplied with loaded tubes on a biannual basis.

1.4.4 Emissions testing reference material

Howard-Reed and Nabinger (2006) described the important characteristics of a reference material. These characteristics included having an independently known emission rate for a particular set of conditions over a reasonable time period, the ability to resemble the mass transfer processes of materials and products commonly used indoors and the emission of a range of VOCs so that both sampling and analytical capabilities are tested.

The development of a possible standard emissions reference material was described by Cox et al., (2010). The material is based on a polymethylpentene film impregnated with toluene and initial results obtained suggest that it is possible to develop a standard reference material with controllable and predictable emission characteristics. Howard-Reed et al. (2011b) have measured the film's emission rates after storage times of up to 6 months. The amount of toluene emitted in the first 24 hours was found to decrease with sample age but, for sampling times of 48 hours and longer, films up to 6 months old would be suitable to assess performance of a chamber test. Inter-laboratory comparison exercises undertaken using the material (Howard-Reed et al., 2011; Howard-Reed et al., 2011a) found, in general, good agreement between toluene concentrations measured for samples of the material tested in different laboratories. Liu et al. (2011) were developing an emission model which after validation was expected to predict the emission profile under a range of experimental conditions.

An alternative design of reference material, reported by Wei et al. (2012a), uses a Teflon cylinder containing a liquid VOC and is described as the "liquid-inner tube diffusion-film-emission (LIFE) standard reference". It was also tested with toluene using a Teflon film to control the diffusion. It was found to have a constant emission rate at a level appropriate for furniture and is expected to be able to be used with other VOCs if suitable films can be found. Wei et al., (2012b) reported that work was underway to develop a related reference material using formaldehyde and for this a film of polydimethylsiloxane was being used.

Horn et al, (2012) described a third design of reference material being developed as part of the EMRP (European Metrology Research Project). Initial work investigated the

addition of four VOCs and two VVOCs to different lacquers which are placed in a μ-CTE. Reproducible emission profiles were obtained for a particular compound and lacquer, with amounts emitted differing between the lacquers. The influence of a range of parameters including temperature and air exchange rate was to be investigated using different emission test chambers.

1.5 Recent developments in sampling and analytical equipment and techniques

1.5.1 Choice of sorbent

As stated previously (Section 1.2.4.2), Tenax TA, is normally used for the determination of the range of compounds defined as 'VOCs' and is the sorbent specified in the normative text of ISO 16000-6:2011. Tenax is the porous polymer 2,6-diphenyl-p-phenylene oxide. It has low artefact levels, efficient adsorption/desorption characteristics and is highly hydrophobic (i.e. it allows water to pass through almost unretained), but it is a relatively weak sorbent. Very volatile compounds were expected to disperse quickly after installation of a product so they were thought unlikely to be of concern. However, VVOCs may continue to be produced for a significant length of time as a result of chemical reactions, such as degradation of additives. Also for multilayer products a coating may slow the VVOC emissions. Similarly SVOC emissions have previously been "considered to present a lower risk" due to their low vapour-phase concentration (Woolfenden, 2009). However, there is substantial evidence of potential effects on health of phthalates esters used to plasticise PVC phthalates (Larsson et al., 2008; Nagorka et al., 2011). This concern has resulted in a trend towards the use of plasticisers of lower volatility (Schossler et al., 2011). There is therefore also a growing demand for the determination of compounds of higher boiling point than those which can be recovered effectively from Tenax TA.

The requirement to increase the volatility range to include both more and less volatile compounds has resulted in interest in the possibility of combining other sorbents with Tenax. One option is to use two or more sorbents in series, either by attaching two tubes containing the individual sorbents required or by packing the sorbents separately in one tube (Markes, 2012). The advantage of the latter method is the possibility of increasing

the volatility range of analytes which can be determined without increasing the cost of measurement. Informative Annex D to the current version of ISO 16000-6 (2011) describes the determination of VVOCs and SVOCs in conjunction with VOCs using a series of sorbents. A schematic of a tube containing multiple sorbents is shown in Figure 1-2. This shows that the direction of gas flow during analysis is the reverse of that during sampling. Seko et al., (2003), for example, investigated the use of a tube containing Tenax TA followed by the carbon molecular sieve Carboxen 1000 for the analysis of VOCs in air and showed it to allow determination of ethanol through to di-2-ethylhexyl phthalate in one run. A disadvantage of carbon molecular sieves, however, is that they exhibit some hydrophilicity, so may need to be purged with inert dry gas after sampling to remove adsorbed water. An alternative might be to employ a graphitised carbon black sorbent. A number of different graphitised carbon black sorbents exist with sorption strengths ranging from weak to medium. Two such sorbents, Carbopack X and Carbograph 5TD, have been developed specifically to give improved strength to organic vapours, while still remaining largely hydrophobic (Woolfenden, 2010b). Multi-sorbent tubes must also be investigated carefully for stability, as delay can cause analytes to migrate from one bed to the stronger bed (Wright et al., 1998). Use of multi-sorbent tubes can therefore offer advantages providing their performance is well defined.

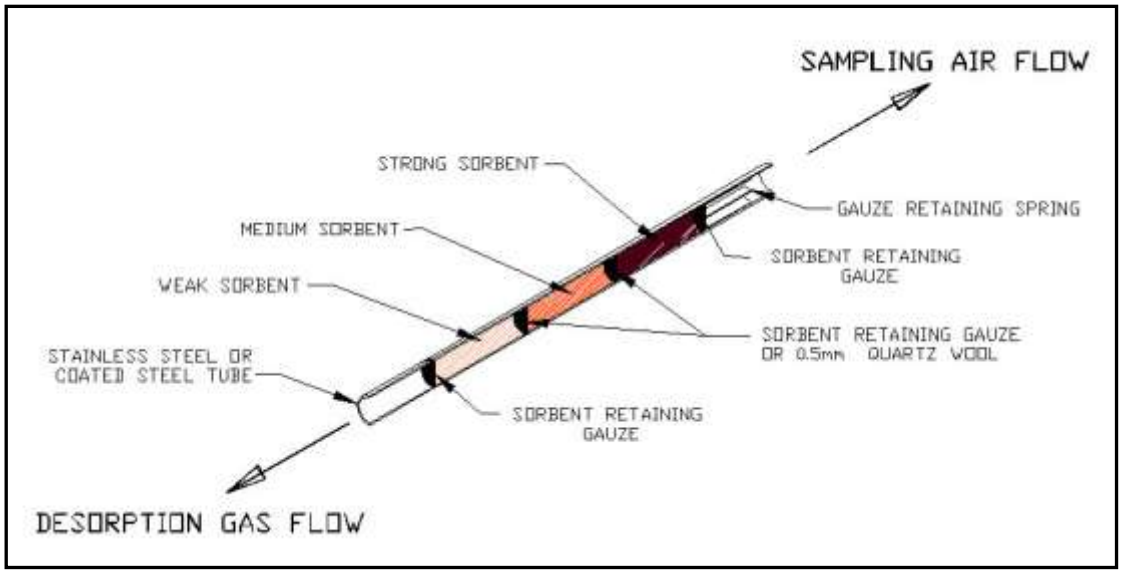

Figure 1-2 Schematic of an air sampling tube packed with three sorbents (supplied by Markes International, 2010)

1.5.2 Possibility of use of TD to determine formaldehyde

A few groups have suggested methods by which formaldehyde, and other volatile aldehydes, might be analysed using thermal desorption followed by GC/MS which would avoid the need for separate analytical instrumentation (typically HPLC) for this group of compounds. It is important that any such method has a low detection limit for formaldehyde as this chemical has a very low permitted concentration, for example in France, AFSSET has proposed indoor air quality guideline values of 50 µg m^{-3} and 10 µg m^{-3} for short-term exposure (2 hours) and long-term exposure respectively (Mandin et al., 2008). Formaldehyde is one of the 10 compounds which are required to be monitored as part of the French building product emissions regulation. In this, a concentration of <10 µg m^{-3} in the reference room will be required for an A+ classification and <60 µg m^{-3} for an A classification (ECA, 2012). There is also increasing concern in the USA about this compound. During 2011 it was listed as a carcinogen by the National Toxicology Program of the US Department of Health and Human Services (Department of Health and Human Services, 2011). In California the Chronic Reference Exposure Level (CREL) value for formaldehyde was lowered from 16.5 µg m^{-3} to 9 µg m^{-3}, with effect from 1st January 2012 (Oppl and Augustin, 2011). A recent study of VOCs in new homes in California found that formaldehyde had by far the highest hazard quotient (ratio of indoor concentration to recommended exposure guideline) of the 22 compounds quantified (Offermann and Hodgson, 2011).

One research group (Ho and Yu, 2004) has proposed coating Tenax with pentafluorophenyl hydrazine (PFPH). This involved mixing Tenax with a known amount of PFPH in hexane. Formaldehyde and other carbonyls react with the PFPH to form thermostable derivatives suitable for subsequent analysis by GC/MS. This technique has been further developed by Chien and Yin (2009) who placed Tenax TA coated with PFPH at the front of tubes and un-coated Tenax at the rear which enabled simultaneous collection of carbonyls and aromatic hydrocarbons. The method was tested with six carbonyls and five aromatics. A collection efficiency of between 94 and 98 % was achieved. A disadvantage of this method, however, is that the Tenax sorbent needs to be removed, recoated with PFPH and repacked for each use. Hermann (2011) reported that further work on this technique was being undertaken at the Claude Bernard

University in Lyon, France. Other groups have investigated the use of the same derivatisation agent, and a second compound, PFBHA [(pentafluorobenzyl)-hydroxylamine hydrochloride], to determine formaldehyde emitted from materials by diffusive sampling (Bourdin et al., 2011; Martos and Pawliszyn, 1998). The principle in this case is solid phase micro-extraction (SPME) and the reagent is coated onto fibres.

A further possible derivatisation agent is 2-hydroxymethylpiperidine (2-HMP) which reacts with formaldehyde to form hexahydro-oxasol[3,4-α]pyridine, also known as 2-oxaindolizidine or formaldehyde oxazolidine. This reaction is used in a NIOSH (National Institute for Occupational Safety and Health) method for the determination of formaldehyde by solvent desorption and GC (NIOSH, 1994). The reagent is coated onto XAD-2 contained in a solid sorbent tube and after air sampling the derivative is desorbed using ultrasonic agitation in toluene. Sampling tubes have been tested in which 2-HMP has been spiked onto Tenax TA then used to sample from a standard atmosphere of formaldehyde, followed by analysis by TD/GC/MS (Veasey, 2000). This work built on earlier studies using the same reagent coated onto a denuder tube which was connected to a Tenax TA tube (Thomas, 1997).

Gu et al., (2010) have suggested the use of a metal-organic framework (MOF) which can trap the formaldehyde without derivatisation. These are hybrid inorganic-organic microporous crystalline materials with a large surface area. One tube was found to suffer no significant loss of collection efficiency over 200 cycles of adsorption/ desorption. The detection limit for the method was found to be 0.6 µg m^{-3} and the quantification limit to be 2 µg m^{-3}. This is comparable with the detection limit of ISO 16000-3:2011 which employs adsorbent cartridges followed by HPLC. The stability of formaldehyde on the sorbent was investigated over periods up to 72 hours and showed a gradual decline to 95 % some 24 hours after sampling and 90 % by 72 hours after sampling, whilst ideally analytes should be stable on a sampler for one week or longer. Also, whilst good performance was found for air samples when relative humidity was less than 45 %, performance decreased dramatically above this value due to competitive sorption of water molecules which would be a problem for emission tests which are to be undertaken at a relative humidity of 50 %.

A further possible method involves deploying a pad or cartridge, impregnated with a derivatising agent, directly upstream of the sorbent sampler. This approach has been used to determine the nerve agent VX by converting it to its more stable G analogue (Woolfenden, 2010a). In this case pads containing silver fluoride are employed. An advantage of such a technique is that the chemical reacts with the derivatising agent as it passes onto the tube and the pad is removed prior to analysis. As a result of this, samplers can be re-used a significant number of times before re-packing of the sorbent is required. The study by Veasey (2000) investigated the impregnation of the 2-HMP reagent into a separate filter placed into the sampling end of the tube and removed before analysis. The method looked promising, but several practical issues have yet to be overcome. It requires further work to determine safe sampling volumes, select the optimum sorbent, optimise the thermal desorption conditions and to study a wider range of formaldehyde concentrations.

1.5.3 Thermal desorption

Optimisation of the analytical performance of thermal desorption for indoor air monitoring was described by Woolfenden (2001). Desorption efficiency of better than 95 % should be achievable for normal VOCs and linearity of systems fitted with a thermal desorber should be comparable to those obtained using normal liquid injection GC methods. The usual way of calibrating TD based methods is to manually introduce standards into sorbent tubes and with this a precision of 1-2 % can be achieved. Developments in TD equipment include automatic leak testing and sealing of tubes before and after analysis to give greater confidence in results obtained and these are now required by international standard TD methods.

More recent models of thermal desorbers have improved designs incorporating shorter path lengths which allow the determination of higher boiling compounds than previously. A range of SVOCs which previously required to be analysed using solvent desorption techniques can therefore now be determined by TD. Recent examples of analysis of SVOCs reported using TD include some personal care products with boiling points between 265 and 392 °C (Ramírez et al., 2010) and a set of PAHs (Wauters et al., 2008). The ability to quantitatively re-collect split flow back onto a sorbent tube for repeat analysis is another more recent innovation in TD (Woolfenden, 2010b). This

overcomes a previous limitation of the technique which was that each sample could only be analysed once.

1.5.4 GC/MS

ISO 16000-6:2011 specifies detection of VOCs using either a flame ionisation detector (FID) and MS or MS only. The MS is required for identification of compounds detected; FIDs have been popular for quantification due to their greater stability and linear range. However use of an internal standard (IS), for example deuterated toluene, can compensate for MS detector instabilities sufficiently to allow routine quantification also to be undertaken with this detector (Demeestere et al., 2008). This avoids the requirement to either split the sample, resulting in lower sensitivity, or to have two TD/GC systems set up with identical sample injection and separation parameters and duplicate sampling to be undertaken.

VOCs present are identified from the retention time of a peak and its mass spectrum. The spectrum is compared with the mass spectra contained in libraries of spectra which may be either commercially available or user-generated. The recommendation in ISO 16000-6 (2011) is that as many compounds should be identified as possible, "particularly those representing the 10 highest peaks and those present at concentrations above 2 µg m^{-3}". A satisfactory level of identification is regarded as having been achieved if the area of identified VOCs when summed corresponds to two-thirds of the total area of all the peaks in the chromatogram eluting between and including C_6 to C_{16}. For some of the labelling schemes, however, (Section 1.3.3) the presence of all compounds on a particular list has to be determined, along with the requirement to determine carcinogens with high sensitivity. The use of selected ion monitoring (SIM) (see Appendix C.3.3), instead of the routinely applied scan mode, is one means of increasing the sensitivity of a mass spectrometric method. A study by Jia et al. (2006), of 94 VOCs found in ambient and indoor air, found improvements of between 1.1 and 22-fold in detection limits using SIM compared to scan mode. However, in the absence of the scan mode it is no longer possible to identify unknown compounds present. One solution to this is to use an MS method which continually alternates between scanning and SIM acquisition modes, in what is known as synchronous SIM-scan. This is an option which has become possible on recent MS models. This approach was used in a

recent study of the emissions from a range of building products undertaken according to the AgBB scheme (Horn et al., 2007). A special method was developed for 38 carcinogenic compounds which enabled their simultaneous determination in one run. Calibration of these compounds was undertaken by preparing solutions with a range of concentrations down to 0.05 ng per injection. 21 of the compounds were found to have a detection limit of <1 ng, 13 had a limit of between 1 ng and 5 ng and four were >5 ng. If a sample volume of 5 litres on Tenax TA is assumed, a detection limit of less than 1 µg m^{-3} was achieved for 89 % of the compounds.

A disadvantage of the SIM-scan approach is that the extra sensitivity can only be obtained for compounds where the SIM parameters have been set up in advance. This can be overcome by use of a time-of-flight (TOF) MS in place of the standard 'quadrupole' type instrument. Scanning analysers, including quadrupole instruments, transmit the ions of different masses successively along a time scale, while the TOF mass analyser allows the simultaneous transmission of all ions. This results in significantly greater sensitivity, at best equivalent to that achieved by a quadrupole running in SIM ionisation mode. TOF technology is based on the accurate measurement of the speed of ions travelling along a flight tube and has become possible with advances in timing electronics. Ions of different mass are separated due to the different speeds at which they travel along the tube. Various flight tube geometries have been developed by different manufacturers in order to optimise the performance. One such is the 'reflectron' which is designed to improve mass resolution by accelerating ions along a path towards an electrostatic reflector or 'reflectron'. At the reflectron the ions are deflected back along the flight tube to the detector.

The reflectron has the capability to correct dispersion in kinetic energy of the ions leaving the source with the same mass to charge (m/z) ratio and it also increases the flight path without increasing the dimensions of the MS (Hoffmann and Stroobant, 2007). Once the ions have reached the detector the flight times are converted into masses using coefficients determined as a result of calibration using a compound which gives ions of known mass. Plate 1-4 shows the flight tube of an instrument based on a reflectron design.

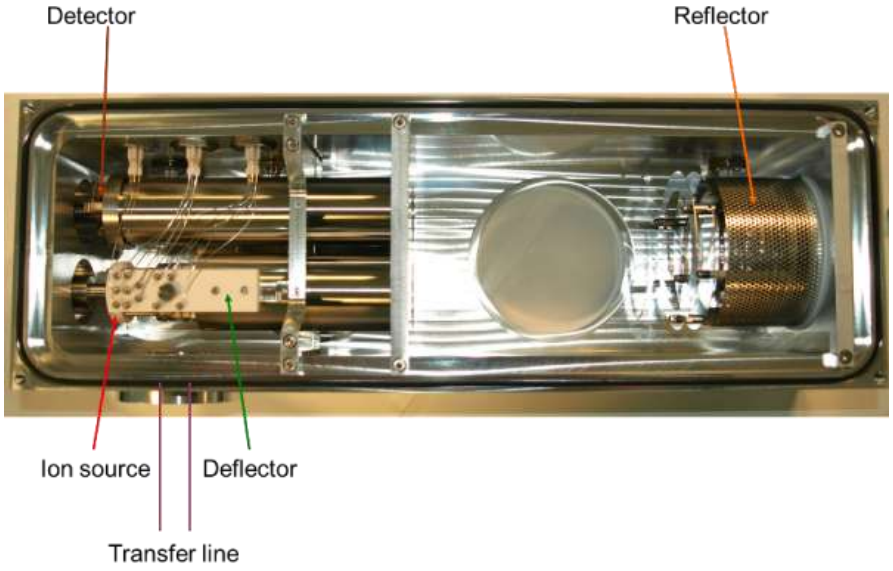

Plate 1-4 The flight tube of a time-of-flight MS based on a reflectron design (supplied by Markes International, 2011)

1.5.5 Analysis software

In a complicated chromatogram with many overlapping peaks, as can be obtained from analysis of the emissions from some materials, identification of all the compounds present can be quite a complex task. Roberts et al., (2009) reported the development of a new chemometric-based software program, TargetView™ (ALMSCO International), to aid the identification of target compounds emitted from a sample. This software processes MS data in a defined series of steps (taken from Roberts et al., 2009):

1. A Dynamic Background Compensation (DBC) algorithm is applied which suppresses mass ions contributing to baseline noise, air/water background, column bleed and anomalies in general. This results in a flatter baseline providing better quantitation, an increase in spectral purity for accurate compound identification and greater signal to noise values for individual compounds.
2. The Total Ion Chromatogram (TIC) is divided into a number of peak positive retention time windows, after which a deconvolution algorithm is applied to each retention time window generating a number of deconvoluted spectra.

3. Principal Component Analysis (PCA) chemometric evaluation of the deconvoluted chromatogram is undertaken. The TargetView algorithm reports a matching co-efficient between the target spectra and the sample.
4. Results are displayed in the form of two plots, showing the original TIC and the compound match co-efficient against peak apex retention time.

The software was applied to the analysis of the emissions from a sample of plasterboard heated at 80 °C in a µ-CTE in order to identify whether the chromatogram showed the presence of any trimethylbenzene (Roberts et al., 2009). This compound was found to occur in the chromatogram as a shoulder to another peak and therefore would have been difficult to identify without this process.

1.6 Aims and Objectives of the project

The growing demand for testing and certification of emissions from building and furnishing products creates a need for economic, fast and reliable test methods to determine the wide range of compounds emitted. The current main approach is to use an emissions test chamber at a temperature of 23 ºC and 50 % RH to determine rates of emission of VOCs and some SVOCs and VVOCs. These values can then be used to calculate the equivalent concentration that would occur in a reference room. The risk to health and well-being due to exposure to the concentration calculated is then assessed and forms the basis of labelling of products with respect to their impact on indoor air quality. A similar approach is increasingly being applied to consumer products. The use of so-called ‘indirect’ or screening methods to complement emission chamber tests is expected to become important for quality control purposes and other in-house tests by material producers. In particular the application of one screening tool (the Markes µ-CTE) at different temperatures to investigate the effectiveness of applying a higher temperature to enhance emissions (to enable problems to be identified during manufacture and remedial action taken) has the potential to be a cost effective and relatively quick method of characterising products. An aim of the study is therefore to optimize methods based on screening tests and thermal desorption/gas chromatography/ mass spectrometry (TD/GC/MS) to determine the chemicals released from such materials and products and included on various target lists.

It is clear that the extensive lists of target compounds that are the subject of frequent revision present a considerable challenge for analytical laboratories, particularly those providing routine analysis for product producers. Therefore there is a need for a robust and as highly automated as possible method for testing and analysis that is applicable to chemicals from the VVOC to SVOC range, with sufficient sensitivity to determine required trace levels of carcinogens within complex matrices of chemicals. A single analysis for all chemicals of interest would result in a significant saving in cost. The possibility of automating the analysis procedure also has the potential to lower costs as less specialised staff would be required.

To further the development of methods for emission testing the following objectives were identified for the project:

1. To examine the benefits and limitations of using indirect/screening methods for testing VOC emissions rather than reference chamber methods.

2. To investigate whether any of the compounds detected on a Tenax TA only tube are compromised by the use of a multi-sorbent tube (which should have enhanced performance for compounds poorly retained using Tenax TA). Tenax TA is currently prescribed in the normative part of European and international standards for determining VOC emissions from building products. While other sorbent types offer some possible advantages, if they are to be applied more widely there is a need to demonstrate equivalence of performance with the compounds determined using the current standard methods.

3. To investigate the possibility of extending the volatility range of compounds that can be determined in material emissions using a sorbent tube and TD/GC approach. Of particular interest is formaldehyde which is a VVOC of concern and currently its determination requires use of a separate sampling and analytical method requiring solvent elution of the sampler and determination by HPLC.

4. To investigate the performance of a TOF MS for the determination of target compounds in material emissions. New developments in TOF MS technology

provide the possibility of future use of the technique as a routine method for characterising product emissions should there be significant advantages over the quadrupole MS now widely applied.

5. To investigate the use of new compound identification software to determine target compounds in material emissions.

The next chapter describes the main materials and methods used in the project, while each of the following five chapters contain work undertaken in support of one of the objectives identified for the project.

2 MATERIALS AND METHODS

This chapter contains information relevant to the project as a whole. Details of more specialist methods used are contained within the relevant chapters or in the appendices.

2.1 Selection of materials to be tested

A range of materials were obtained on which to apply various screening techniques for the testing of emissions in support of objective 1 of the project. The main requirement for the materials selected for testing was that they were representative of the types of materials used within buildings. A range of emissions profiles were also required which would enable a comparison of the effectiveness of different sorbent types for sampling (objectives 2 and 3). The data obtained was also to be used for comparison of manual and automated processing techniques (objective 5). The materials acquired for testing were a mixture of some commercially available and some obtained directly from material producers, with one being obtained from another research group. Two producers provided materials samples, a producer of windows and doors (Producer A) and a producer of wall covering materials (Producer B). An advantage of those obtained from their producers was the possibility of receiving details about the material such as its date of manufacture. Details of the materials tested are as follows:

2.1.1 Materials obtained from producer A

Producer A supplied the following materials:

PVCu 1 – PVCu (Unplasticised polyvinyl chloride) Window Profile sample, extruded using lead based stabiliser, white with a strip of black gasket, manufactured on 24th January 2011 (see Plate 2-1).

PVCu 2 – PVCu Window Profile sample, extruded using calcium organic stabiliser, white with a strip of black gasket, manufactured on 23rd January 2011.

Information was provided that the PVC was composed of the following main raw ingredients: PVCu resin, filler (chalk), impact modifier, stabiliser (either lead or calcium organic) and colour pigment.

Aluminium 1 – Aluminium section, white, window sash which clips onto a PVCu window frame, manufacturing date unknown (supplied by a third party).

Aluminium 2 – Aluminium section, anodised, window sash which clips onto a PVCu window frame, manufacturing date unknown (supplied by a third party).

Composite Door sample – made using PVCu and glass reinforced plastic (GRP) skins and polyurethane (PU) foam insert, off-cut taken directly from production line on 31st January 2011 (see Plate 2-1).

These materials samples were received by post on 15th February 2011 and each material was unwrapped from its packaging and wrapped in aluminium foil and stored in a clean cupboard at room temperature prior to emission testing.

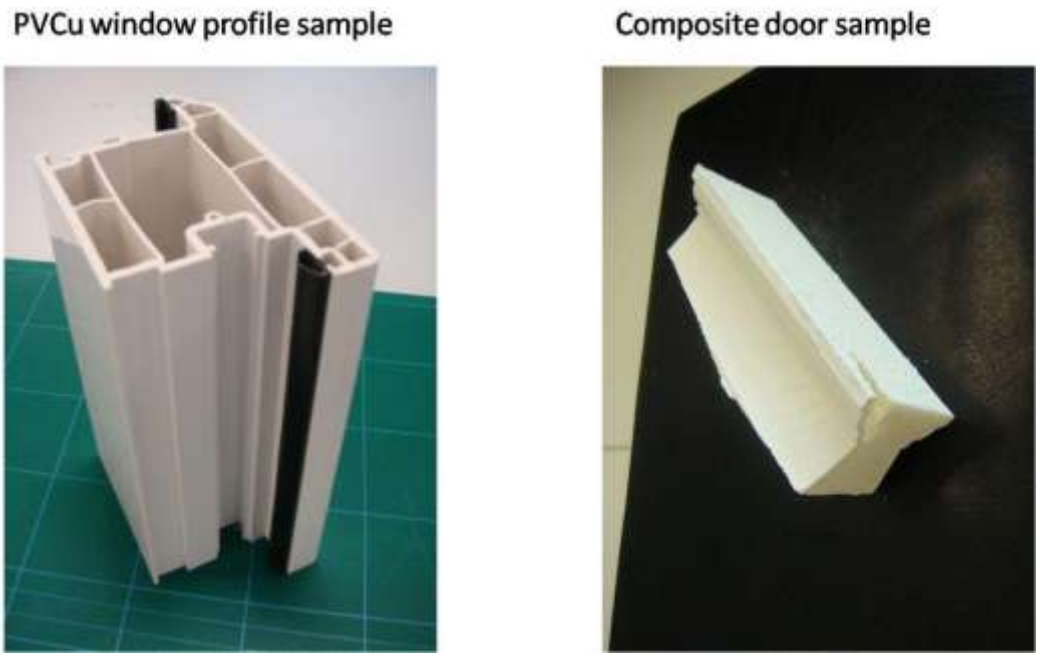

Plate 2-1 Window and door samples supplied by manufacturer

2.1.2 Materials obtained commercially/from another research group

Material A was a 50 cm^2 carpet tile purchased in a local DIY store.

Material B was obtained from a group at the Warwick Manufacturing Group (WMG), University of Warwick. This was a roll of PVC 'leatherette' intended for use in vehicle interiors. This material is very consistent in its manufacture and its morphology

(Warwick Manufacturing Group, 2010). The emissions from this material have been studied by the WMG so this would allow some comparison of the results obtained in the present study.

Material C was a roll of sculptured vinyl wallpaper purchased in a local DIY store.

Material D was a pack of 'value' self-adhesive vinyl floor tiles purchased in a local DIY store.

All these materials were wrapped in aluminium foil and stored in a clean cupboard at room temperature until use.

2.1.3 Materials obtained from producer B

Producer B supplied one roll of each of the following materials which had been placed into plastic bags within five minutes of manufacture:

Wall covering 1: 180 g m^{-2} plasticised PVC screen printed on 110 g m^{-2} paper.

Wall covering 2: 150 g m^{-2} plasticised PVC and water based ink screen printed on 85 g m^{-2} nonwoven base.

Wall covering 3: ~10 g m^{-2} water based ink gravure printed on 150 g m^{-2} paper.

Wall covering 4: ~10 g m^{-2} water based ink gravure printed on vinyl laminate of 90 g m^{-2} plasticised PVC and 90 g m^{-2} paper.

Information was provided that low aromatic (<0.5 %) white spirit 'D40' was used for PVC plastisol viscosity control and that the plasticisers used were diisononyl phthalate (DINP), di-2-ethylhexyl terephthalate (DEHT) and di-2-propylheptyl phthalate (DPHP). The nonwoven base was a mixture of cellulose and polyester fibres in a ratio ~85:15.

These materials samples were received by post on 27th June 2011 and are shown in Plate 2-2. Each roll, still inside its plastic bag, was wrapped in aluminium foil and stored in a clean cupboard at room temperature prior to emission testing.

Plate 2-2 Rolls of wall covering materials as received at Cranfield

2.2 Screening techniques used during the project

Objective 1 of the project sought to examine the benefits and limitations of using indirect/screening methods for testing VOC emissions rather than reference chamber methods. To accomplish this, tests of a range of materials and with a variety of conditions were undertaken using the Markes µ-CTE (introduced in Section 1.3.1.3) and a bag sampling method. A FLEC was also set up in the laboratory and applied as a reference method (see Section 1.3.1.2). Results obtained using these techniques were then used in the comparison of sorbent types (objectives 2 and 3) and the comparison of manual and automated processing (objective 5). Brief details of the three techniques are given in the following sections. Procedures were developed from experience gained in the initial experiments using each technique and these are contained in Appendix A.

2.2.1 µ-CTE sampling

The µ-CTE was connected to a supply of zero grade compressed air and the air supply passed through a charcoal filter immediately before it entered the instrument in order to minimise contaminant levels. Plate 2-3 shows one micro-chamber of the µ-CTE being loaded with a disc of material in surface testing (or 'cell') mode. Sampling tubes are attached to two of the other micro-chambers. A sampling procedure for the use of the µ-CTE was developed and is contained in Appendix A.1. This is based on part 3 of the

standard for emissions of VOCs from automotive vehicle interior parts and materials (ISO 12219-3:2012). The system background was investigated as part of the emissions tests by undertaking several control runs with no materials in any of the µ-CTE chambers. Details of the findings of this background investigation are contained in Appendix B.

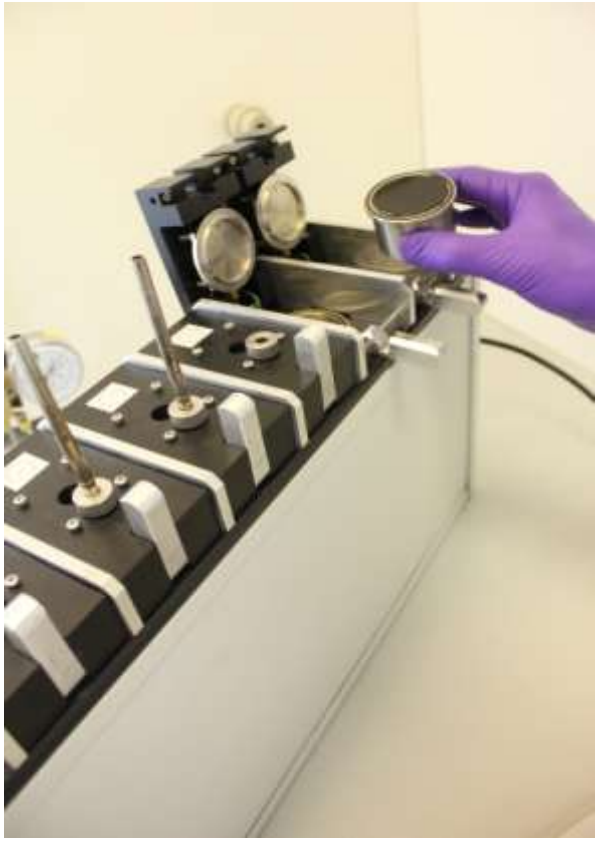

Plate 2-3 µ-CTE being loaded with a material sample

2.2.2 Bag sampling

Bag sampling has been applied as a cost effective screening method for a related product type, namely vehicle interior parts (BS ISO 12219-2:2012). This method involves heating a material sample in a sampling bag and then the gas in the bag is collected to measure the test concentrations. The standard specifies the use of a bag made of an inert, impermeable and non-sorbing material e.g. a fluorinated resin, such as polyvinylfluoride (PVF). PVF (trade name Tedlar) bags are commercially available, but a more economical alternative is to prepare sampling bags in-house. Polyethylene-

terephthalate (PET), trade name ‘Nalophan’, is a material available in rolls that can readily be made into bags and has been used for the sampling of VOCs in human breath (Beauchamp et al., 2008). It is also listed in the CEN standard for the determination of odour by dynamic olfactometry (BS EN 13725, 2003) as being one of the three materials, alongside PVF and FEP (tetrafluoroethylene hexafluoropropylene copolymer), considered appropriate for making sample containers.

ISO 12219-2:2012 specifies heating the bags containing samples of vehicle materials at a temperature of 65 °C. For testing building materials, which are likely to experience lower maximum temperature in use than for materials to be used in vehicles, it was decided to also investigate results obtained at a somewhat lower temperature (40 °C). An incubator was used to heat the sample bags and this is shown set up with a sample and a control bag in Plate 2-4. A sampling procedure was developed as a result of the initial tests of materials undertaken and this is contained in Appendix A.2.

Plate 2-4 Incubator heating sample and control bags

2.2.3 FLEC sampling

In order to determine VOCs emitted from building products and furnishings using a FLEC according to the ISO standard method BS EN 16000-10:2006 the FLEC needs to

be set up with a supply of clean air and using conditions of 23 ± 2 °C and 50 ± 5 %RH. The FLEC was connected to the laboratory compressed air supply through a charcoal filter and an air control unit (FL-1000) which allowed adjustment of the flow and humidity of air supplying the cell. The background was investigated at various points in the system both before and in between each of the first series of tests undertaken using this equipment. The temperature of the laboratory was recorded during tests and an independent check of the humidity supplied to the FLEC by the air control unit made. Finally the recovery of a source of n-dodecane through the system was investigated as specified in ISO 16000-10:2006. Details of all these tests to monitor the performance of the FLEC are contained in Appendix B.

The FLEC was either placed directly onto a material to be tested or, if an air-tight seal was not achieved, within a sample holder. Plate 2-5 shows the FLEC resting on a carpet test plate which was used for a number of the materials tested in the present study.

Plate 2-5 FLEC and air control unit set up in Cranfield Health laboratories

A procedure for sampling VOCs emitted from materials using the FLEC, based on ISO 16000-10:2006, was developed and applied to the testing of material samples. This procedure is contained in Appendix A.3.

2.3 Sorbent tubes

2.3.1 Tube packing material

The majority of analyses undertaken as part of this project used sorbent tubes packed with Tenax TA, while for objectives 2 and 3 the use of multi-sorbent tubes was explored. The sorbent combinations used were quartz wool, Tenax TA and Carbograph™ 5TD (abbreviated as MS1) and quartz wool, Tenax TA and Carbopack™ X (abbreviated as MS2). All tubes were industry standard size (89 mm length and 6 mm O.D.) and were made of stainless steel. As described in Section 1.5.1, the presence of a stronger sorbent at the back of the tube should assist the analysis of very volatile components which are not well retained on Tenax TA alone. Carbograph 5TD and Carbopack X are graphitised carbon sorbents of approximately equivalent strength (Fastyn et al., 2005) and significantly stronger than Tenax TA. They are largely hydrophobic, so should not encounter a problem with water adsorption (Woolfenden, 2010b). The presence of the quartz wool at the front of the tube is believed to assist the analysis of semi-volatile compounds which will be trapped on the quartz and will therefore not reach the Tenax from which they would be hard to remove.

2.3.2 Tube conditioning and storage

Tubes used during the project were supplied newly packed by Markes International Ltd. Before first use, the tubes were conditioned to remove volatile contaminants resulting from manufacture, transport or storage. A procedure for conditioning of the tubes was developed (Appendix A.4) and further conditioning was undertaken before each subsequent use. A log of the number of times each tube has been heated (either analysed or conditioned) was maintained. Conditioned tubes were used within four weeks. When not in use, tubes were kept sealed with brass Swagelok end-caps containing PTFE ferrules. A CapLok™ tool was used to tighten the end-caps (see Plate 2-6). Tubes were normally stored in a sealed plastic box at room temperature, an exception being during stability experiments with the multi-sorbent tubes where the effect of storage at different temperatures was investigated. A proportion of these tubes were stored in a laboratory refrigerator and in this instance end-caps were retightened once the tubes had reached their storage temperature. Refrigerated tubes were removed from the refrigerator and

left to equilibrate at the laboratory temperature before the storage caps were removed for analysis in order to prevent humidity from the air condensing inside the cold tube. Prior to loading onto the TD-100 for analysis the Swagelok caps were replaced with DiffLok™ caps.

Plate 2-6 CapLok tool and sorbent tubes sealed with Swagelok and DiffLok caps

2.4 Analytical equipment

The majority of the analysis for this project was undertaken on the dedicated thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) system which was installed in the Institute of Environment and Health (IEH) volatiles laboratory on the third floor of the Cranfield Health Laboratories in February 2010. This consists of a Markes TD-100™ thermal desorber, an Agilent 6890 gas chromatograph and an Agilent 5973 mass selective detector (MSD). The TD-100 is equipped with mass flow controllers to enable programmable control of gas flows and also has the ability to re-collect the split flow. The TD-100 is connected to the GC with a transfer line which utilises a deactivated fused silica line for the sample path.

The TD-100 is controlled by its own software package (initially version 4.2.21, updated to 4.3.1 in June 2010, to 4.4.1 in December 2010 and to 4.5.2 in September 2012) and the GC/MS by Agilent ChemStation® software version D03. These packages run on the same PC which is located adjacent to the instrument. The complete system is shown in Plate 2-7.

Plate 2-7 TD/GC/MSD system installed in IEH volatiles laboratory

Investigations were also undertaken on the TD/GC/TOF MS system which was installed in the same room in March 2011. This system is composed of a Markes Series 2 UNITY™ two-stage TD and Markes Series 2 ULTRA™ Autosampler, an Agilent 7890 GC and an ALMSCO BenchTOF-dx time of flight (TOF) MS. The thermal desorber features a facility for manual re-collection of split flow and uses needle valves (rather than mass flow controllers) to control split flows. The TOF MS is a reflectron instrument in which ions are extracted from the ion source in a pulsed acceleration region (see Section 1.5.4). The flight tube contains a deflector to bend the ions towards the reflectron. From the reflectron the ions are directed towards the detector which is composed of a series of micro-channel plates.

The system is controlled by ALMSCO ProtoTOF software (version 1.1.1, initially Build 7, updated to Build 9 in March 2012), ALMSCO dx-Connect software (initially version 1.1.13, updated to 2.0 in September 2012), Agilent ChemStation software (version E.02) and Markes UNITY 2 software (version 4.1.29). These packages run on the same PC which is located adjacent to the instrument. The complete system is shown in Plate 2-8.

Plate 2-8 TD/GC/TOF system installed in IEH volatiles laboratory

The BenchTOF-dx is new technology, product literature for which states that it offers "an unrivalled combination of sensitivity, compound resolution, spectral quality and robust operation". This information also states that "uniquely for GC/TOF MS it has the ability to produce 'classical' electron ionisation spectra" (ALMSCO, 2010). These features offer the possibility of the instrument becoming a routine tool of the future if the stated advantages are proven.

For both analytical systems, identification of spectra is aided by the National Institute of Science and Technology (NIST) mass spectral library (2008 version). ALMSCO TargetView compound identification software (see Chapter 7) was also installed on both PCs.

Early in the project a range of experiments were undertaken to develop an optimised analytical procedure for the TD-100/GC/MSD system (see Appendix A.5). Details of thermal desorption, gas chromatographic and mass spectrometric parameters investigated and experiments undertaken in order to develop the analytical procedure are given in Appendix C. This appendix also contains details of work undertaken to demonstrate the performance of the system. These included regular analysis of a quality

control solution (Section C.4.2) and participation in two inter-laboratory comparison exercises during the course of the project (Section C.4.3). Experiments undertaken to optimise the performance of the system incorporating the TOF MS and to demonstrate its application to material emissions testing are described in Chapter 6 and the procedure developed for this system is contained in Appendix A.6.

2.5 Selection of chemicals to be determined

2.5.1 Published target lists for product characterisation

As identified in the literature review, there are several existing lists of chemicals which are of concern due to their emission into air from materials. The first step in deciding which chemicals to determine as part of this project was to obtain the lists of target chemicals specified by a range of international standards and labelling schemes and compare the chemicals listed on each. The lists of chemicals used were obtained from the following sources:

1) Annex A of ISO 16000-6 (2011) which contains a table of examples of compounds detected in indoor air and from building products in test chambers. The list contains 167 VOCs separated into 12 groups of compound types.

2) Annex A of the European standard for assessing emissions from adhesives (EN 13999-1, 2006) which contains a list of examples of carcinogenic and sensitising substances required to be determined in emissions from these products. The list contains 11 VOCs/VVOCs (and two SVOCs) and two aldehydes. Vinyl chloride, which has a boiling point of -13 °C, is included on the list and would require determination using a much stronger sorbent than Tenax TA. Seven isocyanates were also listed, these would be determined using solvent desorption and liquid chromatography.

3) Annex B.2 of the international standard for emissions of VOCs from resilient, textile and laminate flooring (BS ISO 10580, 2010) which contains the requirement to test for the presence of any carcinogenic compound as defined in European Directive 76/769/EEC. prEN 15052:2004, on which this standard is based, includes a list of 137 carcinogenic compounds extracted from Annex 1 of the European Directive 76/769/EEC. The prEN includes a note that the list is only to be considered for volatile

components as defined in ISO 16000-6. From a check of the boiling points of the compounds on this list, 97 of these should be appropriate to be determined by TD analysis.

4) The 2012 version of the "Health-related Evaluation Procedure for Volatile Organic Compounds Emissions (VOC and SVOC) from Building Products" published by the German Committee for Health-related Evaluation of Building Products (AgBB) (AgBB, 2012). The list contains 176 VOCs (and 12 VVOCs/SVOCs) separated into 12 groups of compound types. It should be noted, however, that seven of the entries in fact refer to a group of compounds, for example, "other terpene hydrocarbons", and other entries include more than one isomer, for example, pentanol for which there are 10 isomers, so the number of compounds involved is significantly greater.

5) The 2009 version of the scheme published by the "French Agency for Occupational Health and Safety (AFSSET)" (AFSSET, 2009). This document lists many of the same compounds as on the AgBB list, but with a small number of differences. It includes 165 compounds separated into 12 groups of compound types.

6) The French government's notification to the Commission in 2010 (European Commission, 2010) of the intention to introduce mandatory labelling of VOC emissions from building and decoration products followed by a decree and order in 2011. The order lists 10 individual compounds from the AFSSET protocol, together with four carcinogenic compounds.

7) The report entitled "Environmental and Health Provisions for Building Products – Identification and evaluation of VOC emissions and odour exposure" (Horn et al., 2007). This report contains a list of 38 compounds which were classified as carcinogens belonging to EU category 1 or 2 [Directive 67/548/EEC] and were required to be determined by the AgBB scheme but not represented by a list in the scheme. The authors selected these compounds based on "plausibility, relevance to building products and potential detectability of the substances".

8) The AgBB/DIBt Assessment Mask (ADAM) software tool for collection and storage of emissions data obtained under the AgBB scheme (DIBt, 2010). The May 2010 version of this document contained a list of 200 individual substances which were

classified as category 1 or 2 carcinogens according to Council Directive 67/548/EEC (status August 2009). 54 of these compounds have been "estimated as emission-relevant substances for construction products by DIBt" (DIBt, 2010). An updated version of the tool was released in August 2012 to cover the latest update to the AgBB scheme, but this was not acquired.

9) The emission testing method for California Specification 01350 (Cal01350) (CDPH, 2010). This document includes links to three lists of chemicals containing 'chemicals of concern' which are to "be included as target VOCs for the testing of emissions under this method". The lists are:

i) California Environmental Protection Agency (Cal/EPA) Office of Environmental Health Hazard Assessment (OEHHA) list of "chemicals for non-cancer Chronic Reference Exposure Levels (CRELs)"
ii) "Cal/EPA OEHHA Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65 or Prop 65) lists of known or probable human carcinogens and reproductive/developmental toxins"
iii) Cal/EPA list of Toxic Air Contaminants (TACs). The CDPH document states that "the list includes all substances on the EPA list of Hazardous Air Pollutants plus additional compounds".

Cal01350 states that chemical substances "that are not VOCs (e.g. metals, acids and pesticides) are not required to be analyzed under this standard method". The December 2008 edition of the CREL list contains 100 chemicals, and the CDPH document contains a list of 35 of these which it classes as VOCs (i.e. compounds "that can be analyzed by the sampling and analytical methods specified"). An update to the CREL list was issued in February 2012, but the CDPH document states that the values it contains shall continue to apply until the changes are published in the standard method. The February 2008 edition of the TAC list contains 189 substances, some of which are outside the volatility range defined for a VOC. From a check of the boiling points of the compounds on this list, 128 of these should be appropriate to determine by TD analysis. The TAC list was reviewed in July 2011, but there were no changes in the compounds included. The May 2010 edition of the 'Prop 65' list contains 836 compounds, 192 of which were identified as being appropriate for determination by TD analysis. (An

updated ‘Prop 65’ list was published in February 2013, changes on which have not been investigated for the purposes of the present project).

10) The ANSI/BIFMA (American National Standards Institute/Business and Institutional Furniture Manufacturer’s Association) Standard “Test Method for Determining VOC Emissions” (BIFMA, 2011). The standard lists 16 compounds against which the performance of the analytical system should be routinely validated. These 16 compounds specified all occurred on at least one of the other lists. The standard also states that “selection of specific VOCs to be measured shall be based on the acceptance criteria established by relevant government agencies, certification and other organisations etc.”

11) The CRI’s Green Label Plus program (Hurd, 2009) which specifies a list of 13 chemicals the emissions of which are required to be determined from carpets and 15 chemicals relevant to adhesives. Eight of the chemicals are common to both materials, making a total of 20 chemicals, seven of which are additional to those required by Cal01350.

12) The Greenguard “Standard Method for Measuring and Evaluating Chemical Emissions from Building Materials, Finishes and Furnishings using Dynamic Environmental Chambers” (GEI, 2011). This document refers to lists of chemicals specified in the Cal01350 method and also requires the determination of compounds for which the American Conference of Governmental Industrial Hygienists (ACGIH) have set a threshold limit value (TLV) industrial workplace standard. Early in the project the 2004 edition of the TLV list was referred to, this contained 354 compounds with existing TLVs, 316 of which were identified as being appropriate for TD analysis. (More recently the 2011 TLV list containing updated compounds and values has been referenced; changes as a result of this updated list have not been investigated).

13) The Greenguard website also includes a section where proposed changes to Standards and Test Methods are posted (GEI, 2010b). A proposed change posted on 18 May 2010 (Change Number 4364.72) reported results of a review of chemicals released by 373 office furniture products tested over the three-year period 2007-2010. These tests found 60 compounds occurring frequently in the emissions and a further 59

compounds occurring at a somewhat lower frequency. Many, but not all, of these compounds were included on one of the USA target lists of chemicals.

These information sources resulted in a total of 15 lists of target compounds, the details of which are summarised in Table 2-1. The chemicals on each of these lists were combined onto one list and updated during the project with the release of new editions of some of the lists. A total of 611 chemicals were found to occur on the version of at least one of the target lists added to the combined list. These chemicals are listed in Appendix F.1. Figure 2-1 gives a breakdown of the number of lists on which each chemical appears. This shows that there is some overlap in compounds between the lists, for example benzene occurs on 13 of the 15 lists, toluene and acetaldehyde occur on 11 lists and three compounds (trichloroethylene, ethylbenzene and styrene) occur on 10 lists, but also a significant amount of divergence, for example 251 compounds occur on only one list. The lists also differ in the proportions of different compound types they contain, this is shown in Table 2-2 which uses the categories defined by the AgBB scheme (note that the ‘others’ category includes compounds with more than one functional group).

Table 2-1 Lists of target compounds and dates of current edition

Number	List (and date of update)	Reference
a	Annex A to ISO 16000-6:2011	BS ISO 1600-6:2011
b	Annex A to EN 13999-1:2006	EN 13999-1:2006
c	Carcinogens from 76/769/EEC, Annex B.2 to ISO 10580:2010	BS ISO 10580:2010
d	(German) AgBB scheme, June 2012	AgBB, 2012
e	(French) AFSSET, 2009	AFSSET, 2009
f	French mandatory labelling of emissions, 2011	ECA, 2012
g	Umweltbundesamt (UBA) CMR category 1 and 2, 2006	Horn et al., 2007
h	CMR category 1 and 2 from 67/548/EEC, ADAM, 2010	DIBt, 2010
i	Chronic Reference Exposure Level (CREL), Cal/EPA OEHHA, 2008	CDPH, 2010
j	Toxic Air Contaminants (TAC), Cal/EPA OEHHA, 2008	CDPH, 2010
k	Proposition 65 (Prop 65), Cal/EPA OEHHA, 2010	CDPH, 2010
l	ANSI/BIFMA, 2011	BIFMA, 2011
m	Carpet and Rug Institute (CRI), 2009	Hurd, 2009
n	Threshold limit values (TLV), ACGIH, 2004	GEI, 2011
o	Measurement Target List for furniture, 2010	GEI, 2010b

Table 2-2 Number of each compound type occuring on each of the lists of chemicals of concern in material emissions identified as part of the project

Category	Target List (see Table 2-1for key to lists of chemicals)															
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**n**	**o**	**Total**
1. Aromatic hydrocarbons	29	1	3	31	28	6	1	2	8	11	6	5	7	20	15	44
2. Aliphatic hydrocarbons	30	0	0	6	5	0	0	0	1	2	2	4	1	20	11	43
3. Terpenes	9	0	0	5	5	0	0	0	0	0	0	1	0	2	5	11
4. Aliphatic alcohols	10	0	0	11	9	0	0	0	1	0	0	1	1	15	8	21
5. Aromatic alcohols	2	0	0	3	3	0	0	0	1	7	2	0	1	5	5	11
6. Glycols and glycol ethers	10	4	0	46	38	1	0	0	6	2	5	1	0	12	13	51
7. Aldehydes	18	1	0	18	22	2	0	0	2	3	4	1	4	7	8	25
8. Ketones	10	0	0	9	9	0	0	0	1	4	1	1	0	18	7	23
9. Acids	10	0	0	10	10	0	0	0	0	1	1	0	1	9	4	17
10. Esters & Lactones	19	0	1	23	22	2	0	0	1	7	3	1	2	29	9	48
11. Chlorinated hydrocarbons	11	2	13	0	3	3	6	11	10	27	26	1	0	37	13	46
12. Others	9	3	80	14	11	0	31	41	4	64	142	0	3	142	21	271
Total	**167**	**11**	**97**	**176**	**165**	**14**	**38**	**54**	**35**	**128**	**192**	**16**	**20**	**316**	**119**	**611**

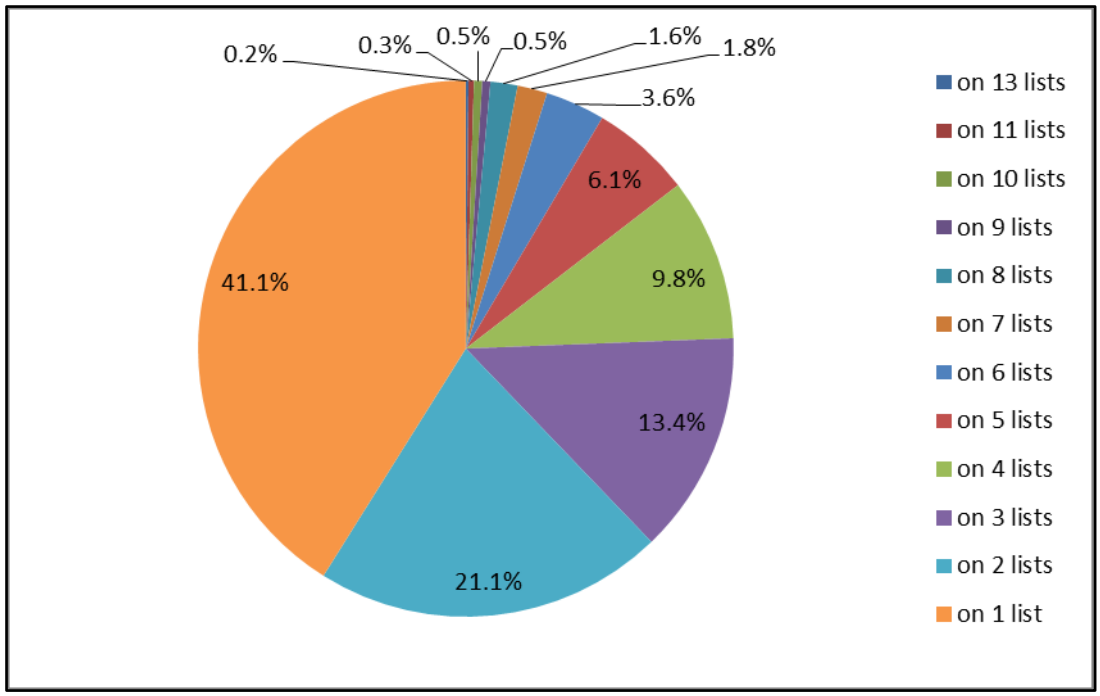

Figure 2-1 Number of the lists of chemicals of concern with respect to material emissions on which each of the 611 chemicals feature (total of 15 lists)

A further list of potentially relevant chemicals is that compiled by a group set up by the European Commission with the title "Expert Group on Dangerous Substances in the field of Construction Products" (EGDS). This so-called 'indicative' list is being updated periodically with a list of substances the Technical committee established by CEN (TC 351) should focus on during the development of harmonised test methods in support of the CPD (EGDS, 2012). It is a compilation of existing national and harmonised legislation within the EU concerning construction products. The May 2009 version of the document included the compounds on the AgBB LCI list, together with 297 substances of concern in Finland, 26 substances from a list of permitted concentrations in residences in Poland and 89 carcinogens of EU category 1A and 1B. After removal of pesticides and those outside the appropriate volatility range, addition of this list would add around 35 compounds to the list generated for this project. A further version of the list was made available in March 2012; compounds on this have not been cross-checked against the project list.

An interesting insight into the relevance of various lists of chemicals of concern to the chemicals that are actually found to be emitted from construction products has been given in a recent review of data on VOC emissions from a range of product types over a 20-year period in the USA (Englert and Black, 2011). They found that greater numbers of chemicals have been detected with time due to an increase in the number of products tested and improvements in analytical and chamber testing technology. Products, however, have generally been found to emit lower levels of chemicals over the years. On comparison of the compounds found against a number of target VOC lists, they found some criteria lists, e.g. LCI and TLV (Threshold limit value) lists, to be more relevant to product emissions than others e.g. prop 65 list, but no list was found to completely capture all product emissions. More recently criteria lists have been found to only partially cover product emissions and this was thought to be due to changes in raw materials and manufacturing processes.

2.5.2 Experimental work

A number of compounds representing the range of lists, boiling points and compound types were acquired at the outset of the project and analysed on the TD-100/GC/MSD system. In particular a 50 component 'indoor air standard' supplied by Supelco (part of Sigma-Aldrich Company Ltd., Gillingham, Dorset, UK) was acquired to assist with development of the method. Compounds analysed were added to a ChemStation user library to assist with identification of unknown peaks in chromatograms.

Several further mixes of compounds were prepared using the procedure described in Appendix A.5. The solutions were diluted to give eight levels covering the concentration range 1 to 3,000 ng μl^{-1}. A solution containing 100 ng μl^{-1} of fully deuterated toluene (d8-toluene) in methanol was prepared separately to act as an internal standard (IS). As noted in Section 1.5.4, use of an IS which is added both to calibration and unknown samples corrects for minor variations in the response of the instrument. An isotopically labelled target compound makes a suitable IS as it will not be found in real samples and can be distinguished from the target compound by its ions (Agilent Technologies, 2005). 1 µl aliquots of each standard solution were analysed in duplicate together with 0.5 µl of the IS solution. Quantification was by determination of the peak area for each compound using an appropriate ion. Calibration curves of response versus

mass on the tube were then produced within the ChemStation software covering the linear range for each compound. As an example the calibration curve obtained for toluene is shown in Figure 2-2. Responses are recorded relative to that for the mass 98 ion of d8-toluene, so the axes represent ratios to the d8-toluene values.

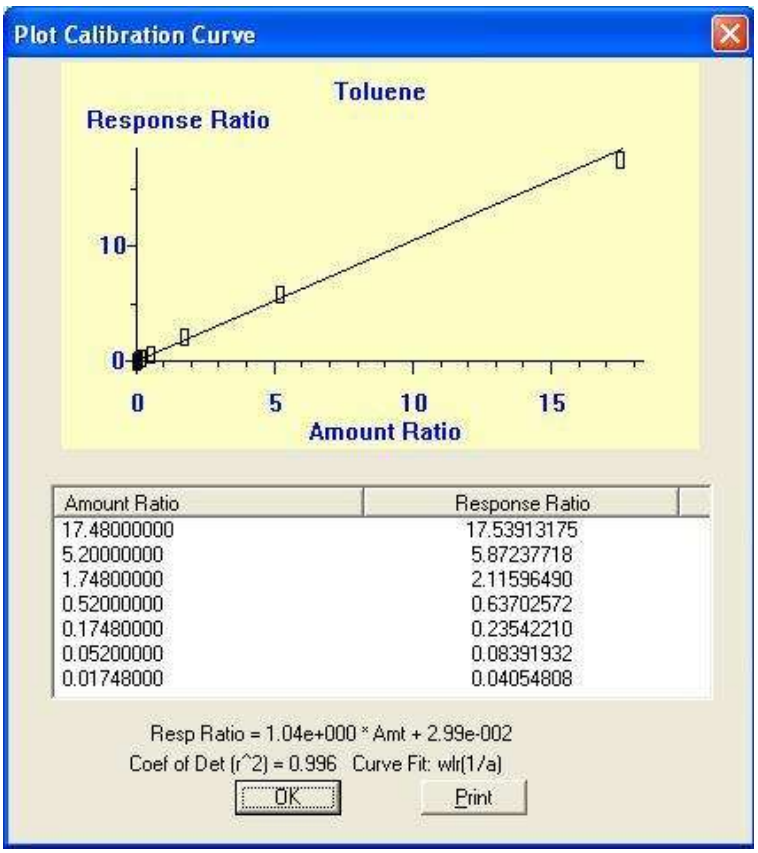

Figure 2-2 Calibration curve for toluene produced within ChemStation software

Further significant compounds emitted from the materials studied as part of the project and occurring on at least one target list were acquired and analysed during the course of the project. A full calibration was undertaken on at least one occasion for a total of 92 compounds. A further 28 compounds had their retention times recorded and for these the calibration factor for toluene was applied, which gives an approximate concentration. These compounds are described as being 'semi-quantified'. Calibration for the 11 compounds selected as 'check standard' compounds for their relevance to material emissions (see Section 1.4.1) was undertaken more regularly. Performance of the system was monitored through daily analysis of this mixture during periods of

operation. Quality control charts were set up for compounds contained in the mixture (see Appendix C.4.2).

The complete list of 120 compounds analysed on the system, together with their retention times and boiling points, is given in Appendix F.2. These represent approximately 20 % of the total number of compounds appearing on at least one target list and at least 10 % of those from each list. Compounds of volatility ranging from acetaldehyde (boiling point 21 °C) to di-2-ethylhexyl phthalate (boiling point 384 °C) have been analysed (though acetaldehyde is a VVOC and will therefore not be quantified with high accuracy using the standard VOC method, possible improvement to its determination is investigated in Chapter 5).

3 EXAMINATION OF THE BENEFITS AND LIMITATIONS OF USING SCREENING METHODS FOR TESTING EMISSIONS FROM MATERIALS

3.1 Introduction

Three sets of tests were undertaken to compare the performance of the selected screening techniques in support of objective 1 of the project. In the first set of tests, emissions from a range of materials were investigated using the Markes Micro-Chamber/Thermal Extractor (µ-CTE) set at two different temperatures. Many reported tests using this screening technique for the testing of building materials, for example those undertaken by Lor et al. (2010a), have used a temperature of 23 °C, as is used in the larger scale emissions tests. An alternative approach is to apply an elevated temperature in order to reduce test times. For example, an ASTM method "for rapid screening of VOC emissions from products" (D7706-11), which was published during the course of the project, suggests the use of a temperature within the range 30-60 °C (ASTM, 2011). In the second set of tests, emissions from four materials were investigated using the µ-CTE and Nalophan bags. These tests were based on conditions employed for screening of emissions from vehicle parts. In the third set of tests, emissions from a further five materials were investigated using the µ-CTE and the FLEC. While also a screening technique, results obtained using the FLEC have been found to correlate well with tests using emissions chambers (as described in Section 1.3.1.2). In the present project the aim was therefore to investigate the conditions which give the best correlation between results obtained using the FLEC and the µ-CTE.

3.2 Methods

3.2.1 µ-CTE tests at two different temperatures

This set of tests was undertaken on portions of a range of door and window materials. These were supplied by the producer shortly after their manufacture (see Section 2.1.3 for details). Duplicate portions of each material type were tested in the µ-CTE at 23 °C and a further two portions at 40 °C. Sampling was undertaken as promptly as possible and was completed within 10 weeks of manufacture for all these materials. Shortly prior

to each test, samples were cut from the materials and weighed then re-sealed in aluminium foil until insertion into a µ-CTE chamber. Separate samples of the two PVCu window profiles were tested with and without a length of gasket. Samples of door segment were cut to give separate samples of polyurethane foam insert and of the front and rear surfaces in order to identify which part of the material is responsible for any emissions observed. The masses of PVCu and aluminium tested were each between 4 and 10 g and those of the foam insert were between 1.1 and 1.3 g. For the samples taken from the surface of the door segment the µ-CTE was operated in surface mode so that emission from the outer surface of each sample could be tested. The remaining samples were tested in the bulk mode.

Before starting the first test the µ-CTE was tested with all chambers empty, then for each test a different chamber was used as the control as a check on cleanliness of the instrument. The µ-CTE was allowed to equilibrate at the temperature of the experiment before adding the material samples, and then the first air sample was taken immediately after addition of a sample to a µ-CTE chamber. Air samples were taken using Tenax TA tubes and a flow rate of 50 ml min^{-1} of air through each µ-CTE chamber. For these tests two successive 15 minute air samples were taken from each chamber (giving an air sample volume in each case of 1.5 litres). More details of the sampling procedure are given in Appendix A.1. The sampled tubes were analysed using the TD-100/GC/MSD system with the procedure described in Appendix A.5.

3.2.2 Comparison of µ-CTE and Nalophan bag tests

Three commercially obtained materials and one obtained from another research group were used for this set of tests. Details of the materials (identified as Materials A-D) are given in Section 2.1.1. These materials were all flat so the µ-CTE tests were undertaken in surface mode. A flow rate of 50 ml min^{-1} of air through each µ-CTE chamber was applied. One test of each material was undertaken at 65 °C, which is the temperature specified in the standard screening method for the determination of the emission of VOCs from vehicle interior parts and materials using micro-scale chambers (ISO 12219-3:2012). It was felt that a lower temperature may be more appropriate for building materials, which are likely to experience lower maximum temperature in use that for materials to be used in vehicles, so a further portion of each material was tested

at 40 °C. The material sample and the µ-CTE were allowed to equilibrate for 20 minutes at the temperature of the experiment, after which time one or more sequential 10 minutes air samples were taken. Fresh portions of each of these materials were also tested in Nalophan bags as described in the sampling procedure in Appendix A.2. Sample and control bags were heated for two hours at either 40 °C or 60 °C (the maximum temperature of the incubator used), then one or more 1 litre air samples were taken using sorbent tubes packed with Tenax TA. Sampled tubes from both the µ-CTE and bag tests were analysed using the TD-100/GC/MSD system.

3.2.3 Comparison of µ-CTE and FLEC tests

Four wall covering materials obtained from their producer were tested using the µ-CTE and the FLEC. With the µ-CTE, six replicate samples of each material were tested. Sorbent tubes packed with Tenax TA were used to sample from three of the chambers and tubes packed with a 3-bed sorbent (Quartz/Tenax TA/Carbopack X) were used to sample from the other three chambers. This was to enable a comparison of sorbents (see Chapter 4). For each material one test was undertaken with the µ-CTE set at 23 °C and one with it set at 40 °C. Shortly prior to each test, samples were cut from the materials and re-sealed in aluminium foil until insertion into a µ-CTE chamber. For these tests the µ-CTE was allowed to equilibrate at the temperature of the test with a flow of air at 50 ml min^{-1} passing through each chamber then an air sample was taken as soon as the material had been added to the chamber. At least two successive 15 minute air samples were taken with extra sets of samples being taken in some runs to enable closer comparison with the FLEC results. The µ-CTE was operated in surface mode for all these tests. Several control runs were undertaken throughout the period with no materials in any of the µ-CTE chambers.

Using the FLEC, each of the wall covering materials were tested in turn according to the sampling procedure described in Appendix A.3. The standard specifies that duplicate samples should be taken at 72 (±2) hours and 28 (±2) days after the start of the test. For this work additional samples were taken earlier in the test to enable closer comparison with the results of the µ-CTE experiments. Each sampling was either undertaken in duplicate using one sorbent tube packed with Tenax TA and one tube packed with the 3-bed sorbent (Quartz/Tenax TA/Carbopack X) or using the two sorbent types

sequentially (depending on the availability of sampling pumps). Results obtained for the two sorbent types are investigated in Chapter 4. A pair of control samples was taken once the air flow had been started and before each material was added to the FLEC, in order to check the background of the system. These control samples were taken with the FLEC resting either on the empty test plate or on a clean piece of aluminium foil. The material to be tested was then unwrapped and a sample cut and placed under the FLEC. Wall coverings 1-3 were found to cause leakage of air from the FLEC (i.e. the outlet air flow from the FLEC reduced significantly when a sample of the material was placed under it). For this reason circles of these materials were instead cut to fit inside the base plate (for wall covering 1 and 2) or just inside the FLEC sealing O-ring and supported on a clean piece of silver foil (for wall covering 3). Wall covering 4 was found to seal onto the FLEC without any reduction in flow through the system. The differences in the sealing of these materials was thought to be due to the pattern on wall coverings 1-3 resulting in an irregular surface to the material, while covering 4 was un-patterned (see Plate 3-1).

Plate 3-1 Two of the wall coverings tested which required different sampling techniques with the FLEC

Air samples were taken immediately after the material had been added and then periodically during the first three days of testing. The material sample was then removed from the FLEC and placed on a piece of aluminium foil in an open box in the laboratory. A further piece of foil was placed loosely over the box to act as a dust shield while allowing flow of air over the sample. The material sample was returned to the FLEC 27 days after the start of the test to allow 24 hours equilibration before the 28 day sampling. All tests (with the exception of a repeat test on wall covering 1) were

completed within four months of manufacture of the materials. The sampled sorbent tubes were analysed using the TD-100/GC/MSD.

Further µ-CTE and FLEC tests were undertaken on portions of a commercially obtained vinyl floor tile. This material was the same product, but from a different batch, as that tested using the µ-CTE and Nalophan bags. For this material a µ-CTE test was undertaken at 40 °C only and the run was continued for two hours with the sampling tubes being replaced each 15 minutes. The purpose of this was to investigate whether sampling after a longer period of exposure in the µ-CTE gave closer results to those obtained using the FLEC.

3.3 Results and Discussion

3.3.1 µ-CTE tests at two temperatures

The chromatograms obtained from analysis of the control air samples (empty chamber) showed a few small peaks which were found to be due to artefacts of the sorbent. No further VOCs were found in the chromatograms from the anodised aluminium, white aluminium or either of the PVCu window profiles (without gasket) tested either at 23 °C or at 40 °C. Both PVCu materials which included a length of gasket gave a number of peaks in each of their chromatograms which were not seen in the controls. A chromatogram from one of these samples tested at 23 °C is shown in Figure 3-1, while those from the other PVCu material (including gasket) gave the same pattern of peaks. These two materials differ only in the stabilisers used in the extrusion process; PVCu 1 using a lead based stabiliser and PVCu 2 a calcium organic stabiliser. Samples of both these materials tested at 40 °C gave the same peaks as observed at 23 °C, all with higher abundance than at the lower temperature (Figure 3-2).

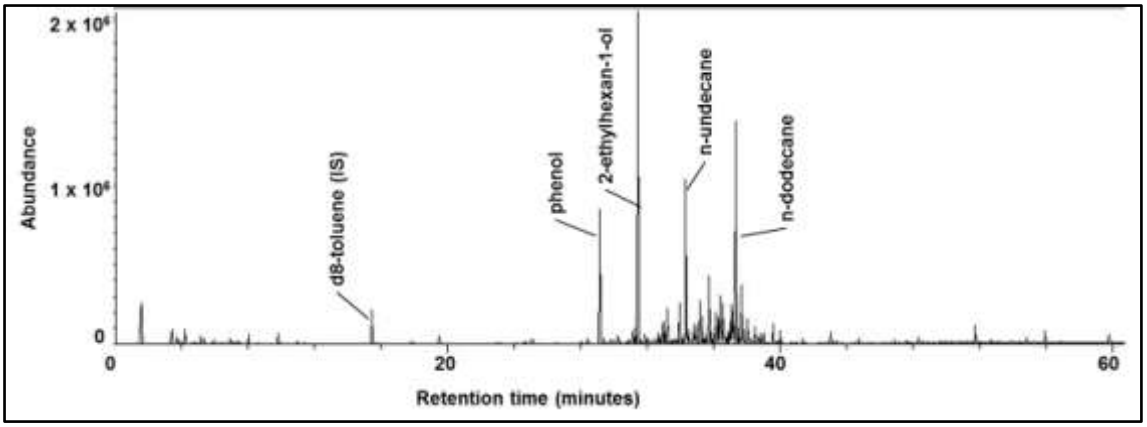

Figure 3-1 Chromatogram from sample of PVCu 1 including gasket tested in the µ-CTE at 23 °C

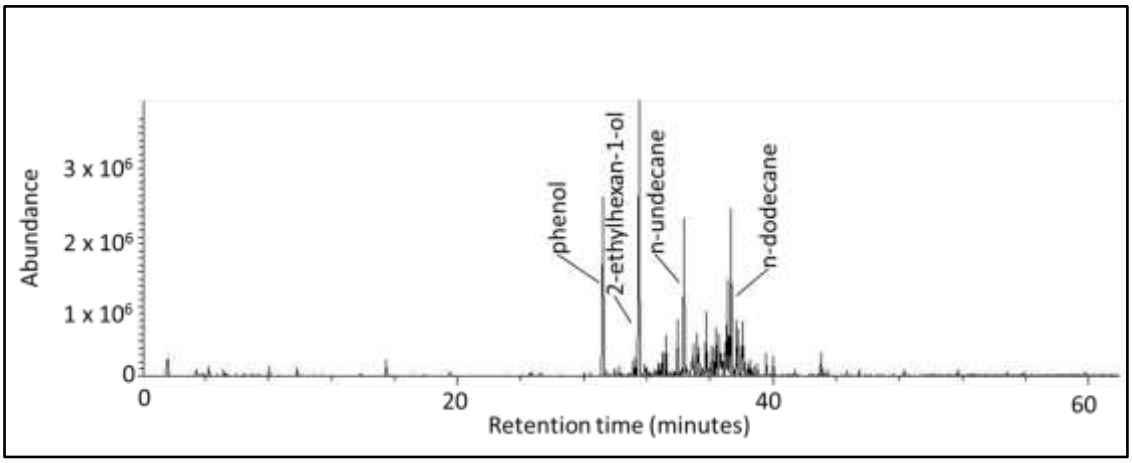

Figure 3-2 Chromatogram from sample of PVCu 1 including gasket tested in the µ-CTE at 40 °C

The amounts of dominant compounds identified in the chromatograms were converted into emission rates by taking into account the mass of each sample and the air sampling time using the calculation described in the procedure for this technique (see Appendix A.1). Emission rates calculated for three dominant compounds from the PVCu 1 samples including gasket are shown in Figure 3-3. These values have been corrected for amounts of VOCs found in a control chamber. The figure also shows amounts of total VOCs (TVOCs) as specified in the international standard for the determination of VOCs in indoor or test chamber air, ISO 16000-6:2011 (see Section 1.2.4). The first and second tubes are the sequential 15 minute air samples taken from one chamber. There is a tendency for higher emission rates of individual compounds and TVOCs during the

second 15 minute period than the first period immediately after the material had been introduced into the chamber. The mean differences ranged between -5 % for n-undecane to 40 % for phenol. Sample 1 and 2 are the two portions of the same material placed in different µ-CTE chambers. The % difference in emission rates for material samples tested at the same temperature was found to vary between 6 % (for phenol from the two samples tested at 23 °C) and 86 % (for n-undecane from the two samples tested at 40 °C).

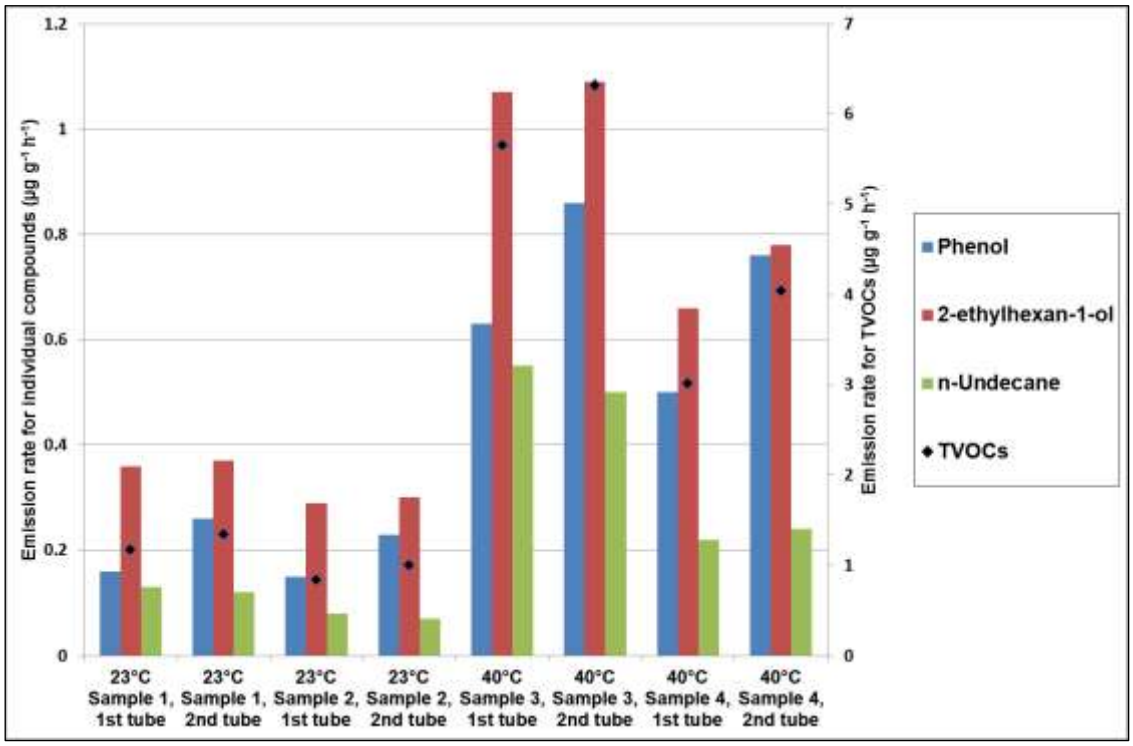

Figure 3-3 Dominant compounds emitted from PVCu 1 including gasket tested in the µ-CTE

The emission rates obtained for the PVCu material extruded using a calcium organic stabiliser (identified as PVCu 2) are shown in Figure 3-4. This material was found to give very similar results to those found for the material extruded using a lead based stabiliser. This is not unexpected as no compounds were detected in the emissions from either of these materials tested without the gasket and therefore it is the gasket which is the source of the emissions.

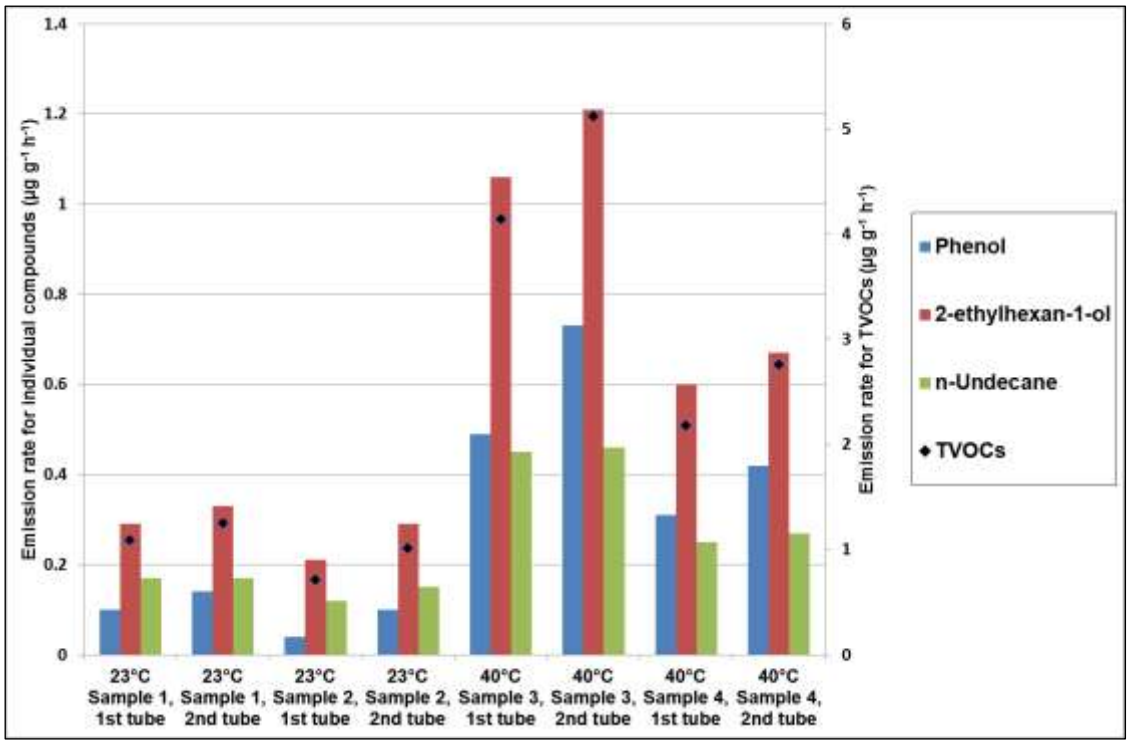

Figure 3-4 Dominant compounds emitted from PVCu 2 including gasket tested in the µ-CTE

The chromatograms from the polyurethane foam samples taken from the door segment gave a different profile. Figure 3-5 shows the chromatogram obtained from one of these samples tested at 23 °C. The dominant compounds emitted from this material were n-pentane, methylcyclobutane (MCB) and styrene. Samples tested at 40 °C gave the same peaks at broadly similar abundances for this material. Emission rates obtained for TVOCs and for dominant individual compounds from foam samples at the two temperatures are shown in Figure 3-6. N-pentane and MCB are classified as very volatile organic compounds (VVOCs) for which a sample volume of 1.5 litres is expected to have resulted in breakthrough of these compounds using Tenax TA, so the amounts found for these compounds are likely to be underestimated. These compounds are not included in the TVOC value. Possible improvements to the method to enable quantitative determination of these compounds are discussed in Chapter 5. MCB has not been analysed on this system and was identified using the NIST library, so it is described as semi-quantified and its emission rate has been calculated using the response factor for toluene as recommended in ISO 16000-6:2011.

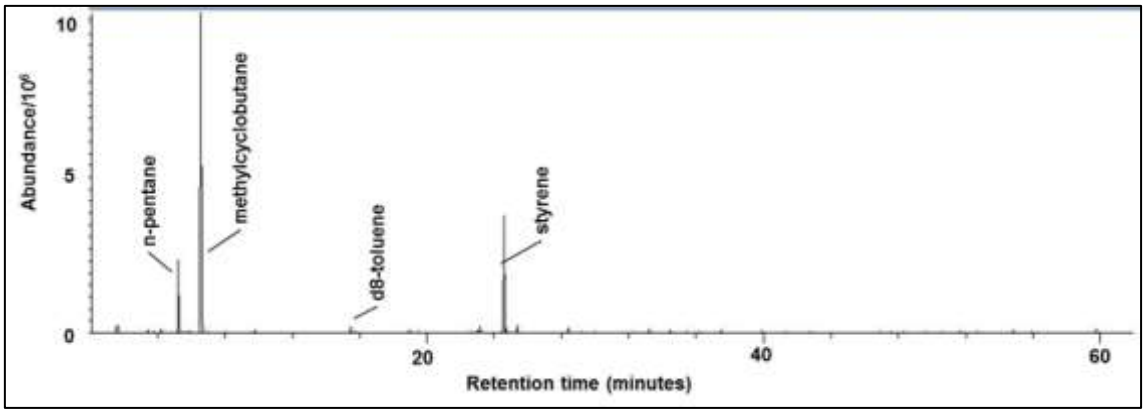

Figure 3-5 Chromatogram from sample of polyurethane foam door insert tested in the μ-CTE at 23 °C

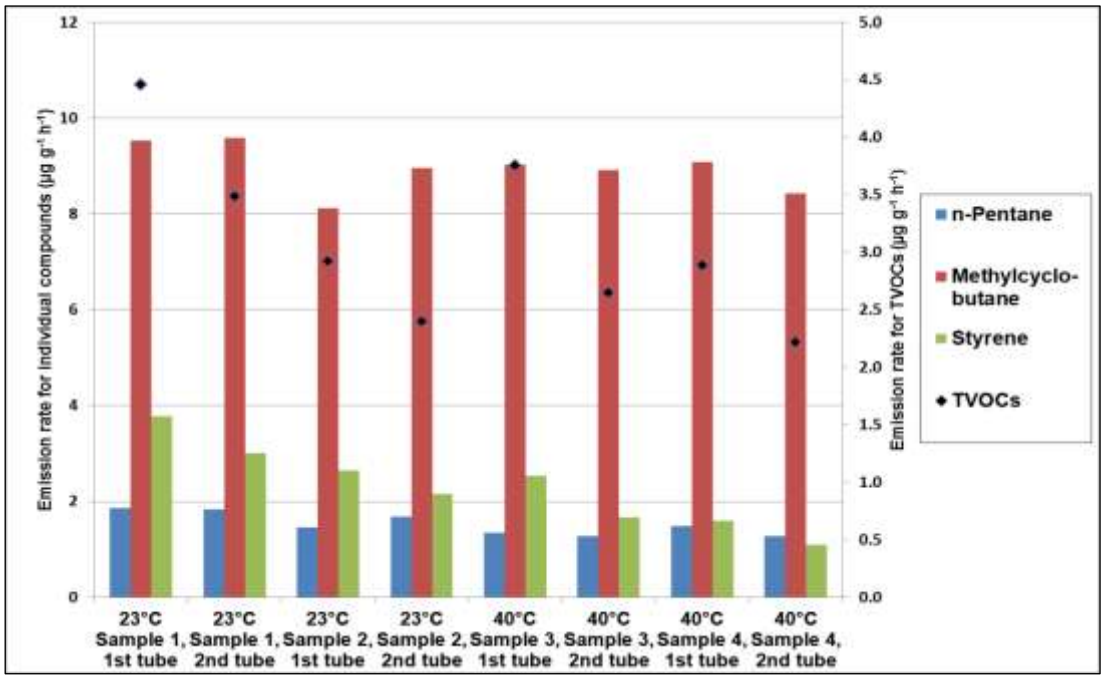

Figure 3-6 Dominant compounds emitted from door foam tested in the μ-CTE
(n-pentane and methylcyclobutane (MCB) are VVOCs so amounts found likely to be underestimated, MCB is quantified using response factor for toluene)

For these samples the emission rates were found to be either similar or slightly lower for the second air sampling periods. The % difference in emission rates for two portions of foam tested at the same temperature was found to be typically between 10 and 30 %.

The chromatogram obtained from analysis of one of the composite door surfaces tested at 23 °C is given in Figure 3-7. This shows, in common with the foam samples, the presence of MCB and styrene. As the foam and the door surface have been in close

contact, it is not unexpected that there is some cross-contamination; the MCB is likely to have been used as a blowing agent in production of the foam, while the styrene is more likely to have originated from the GRP (glass reinforced plastic) in the door surface material. Several other compounds, including methyl isobutyl ketone, toluene, butyl acetate and xylenes, are also observed in smaller amounts in the emissions from the door surface. The same range of compounds was observed from the door surface samples tested at 40 °C.

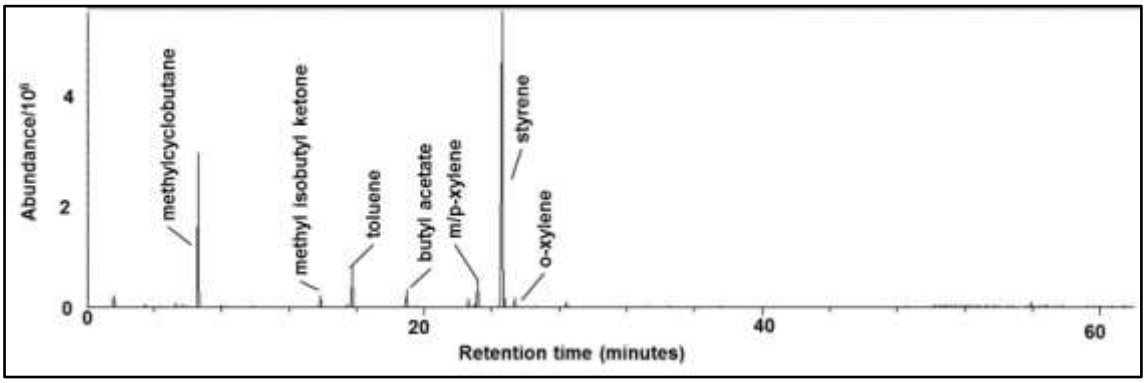

Figure 3-7 Chromatogram from sample of composite door surface tested in the µ-CTE at 23 °C

Emission rates for TVOCs and dominant individual compounds from samples of the first door surface tested are given in Figure 3-8 and those from samples of the other door surface are given in Figure 3-9. As these samples were subjected to surface emissions testing, these emission rates are given as mass per unit area. The styrene peak was found to be above the linear range of the instrument, so the amounts of this compound determined may be underestimated. These samples gave higher emission rates for each compound from the second air sampling period than the period immediately after the material had been introduced into the chamber. The % difference in emission rates for two portions of this material tested at the same temperature was found to be typically between 20 and 40 %.

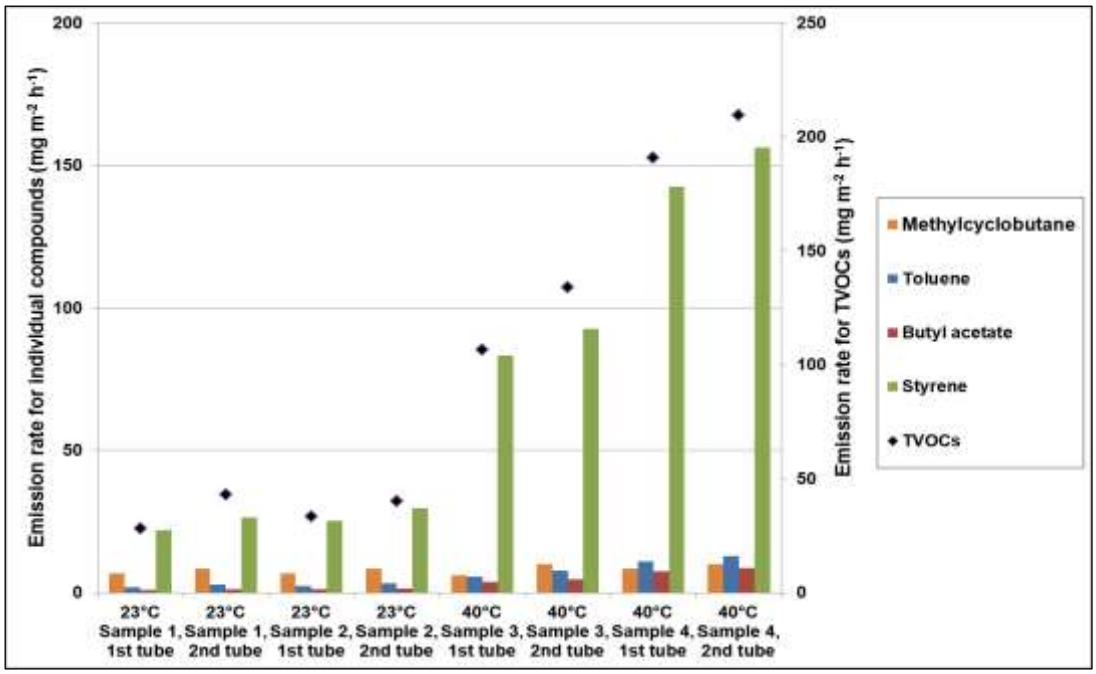

Figure 3-8 Dominant compounds emitted from door surface 1 tested in the µ-CTE
(response for styrene above top of calibration curve so amount may be underestimated)

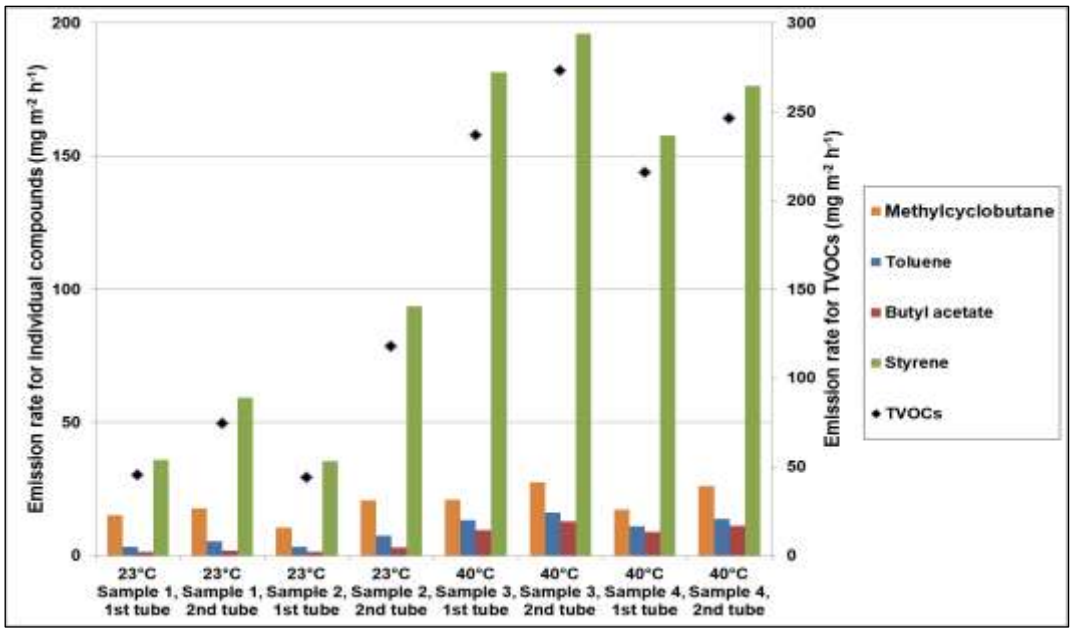

Figure 3-9 Dominant compounds emitted from door surface 2 tested in the µ-CTE
(response for styrene above top of calibration curve so amount may be underestimated)

In these tests the PVCu window profile and composite door samples were found to emit greater amounts (~2-5 times) of VOCs at 40 °C than at 23 °C. The emission profile in each case was not distorted significantly, and no major extra peaks were observed at the

higher temperature. This suggests that the use of a slightly elevated temperature can increase the sensitivity of screening tests and the speed at which results can be obtained. The results for the door foam samples did not follow this pattern, with similar amounts being observed at 23 °C and at 40 °C. The compounds released in this case (other than the styrene which is thought to have come from the GRP) are VVOCs used as the blowing agent in the production of the foam. In use this material is sealed within the PVCu/GRP and the sample preparation procedure has resulted in an initial high emission from the cut surface of the material. The use of a slightly elevated temperature in screening tests of material emissions is recommended in two standard methods published during the course of the project, a method for determining emissions from car interior trim components (ISO 12219-3:2012) and ASTM method D7706-11 "for rapid screening of VOC emissions from products" (ASTM, 2011). The optimum temperature to use will be investigated further in the next two sections.

These two standard methods also include a recommendation to use an equilibration period before taking a sample during these screening tests. For the materials tested here, again with the exception of the foam, the amounts of compounds found on the second tube were slightly higher than those for the first tube, showing this recommendation to be appropriate. A previous study of emissions from a range of materials using the μ-CTE by Schripp et al. (2007) also found a conditioning time of 15 minutes allowed the emission rates to stabilise when testing a material used in computer monitors and in the automotive industry (an acrylonitrile-butadiene-styrene plastic).

The % differences obtained between duplicate samples give a measure of the variability which can occur due to inhomogeneity in the materials, as well as the uncertainty of the test method. The small size of the sample can be advantageous for increased understanding of the source of emissions through comparison of emissions from different areas of a material or components of a product. ASTM D7706-11 states that "duplicate results should agree within 25 %, depending on sample homogeneity", though few studies have reported repeatability obtained for materials emission studies. Good repeatability was found for some of the materials tested in the study by Lor et al. (2010a), but higher results for a linoleum floor covering and an insulation material were thought to demonstrate inhomogeneity in these materials. Repeatability of results

obtainable from screening tests of a range of materials is investigated further as part of the present project (Section 3.3.3).

With these tests the µ-CTE has been found to be a quick and easy way to provide information about the emissions from the products. It has been shown to identify materials without emissions which will not require testing under the CPR (although it is possible that some materials, such as those containing just untreated metal, may avoid the requirement to undergo emissions testing on the basis of their zero VOC content). For materials which emit VOCs it has shown differences in the emissions, which suggests that it could be used to pinpoint the source of the emissions. The chemical of particular concern identified in the emissions from these materials is styrene, which is believed to originate from the GRP in the portions of composite door tested. This compound occurs on 10 of the 15 lists of chemicals of concern in material emissions identified as part of this project (see Section 2.5). The author is not aware of any published studies of the emissions from PVC window profiles or composite doors. Crawford and Lungu (2011), however, have studied the emission of styrene from a "vinyl ester resin thermoset composite material" due to concern about its emission from this type of material with possible resulting adverse health effects.

3.3.2 Comparison of µ-CTE and Nalophan bag tests

3.3.2.1 Material A (Carpet tile)

The chromatogram obtained on analysis of the first Tenax TA tube used to sample air from the µ-CTE containing a portion of material A heated at 40 °C is shown in Figure 3-10 (blue trace). This figure also shows the chromatogram obtained on analysis of a control tube i.e. a Tenax TA tube used to sample from the µ-CTE once it had equilibrated at 40 °C, but before the material sample had been inserted (inverted black trace). The material sample gave many peaks in the chromatogram that represent compounds of a wide range of volatilities and these occur over a wide range of concentrations. Some peaks are also observed in the control chromatogram, analysis of a blank tube (i.e. a conditioned Tenax TA tube which has had no air passed through it) shows that the bulk of these peaks are artefacts of the sorbent (e.g. benzene at retention time [RT] 9.80 minutes). This means that the µ-CTE chamber and the supply air were

clean. The test of a portion of this material heated in the µ-CTE at 65 °C gave a similar pattern of peaks, with greater absolute amounts and a shift towards greater relative amounts of the higher boiling compounds.

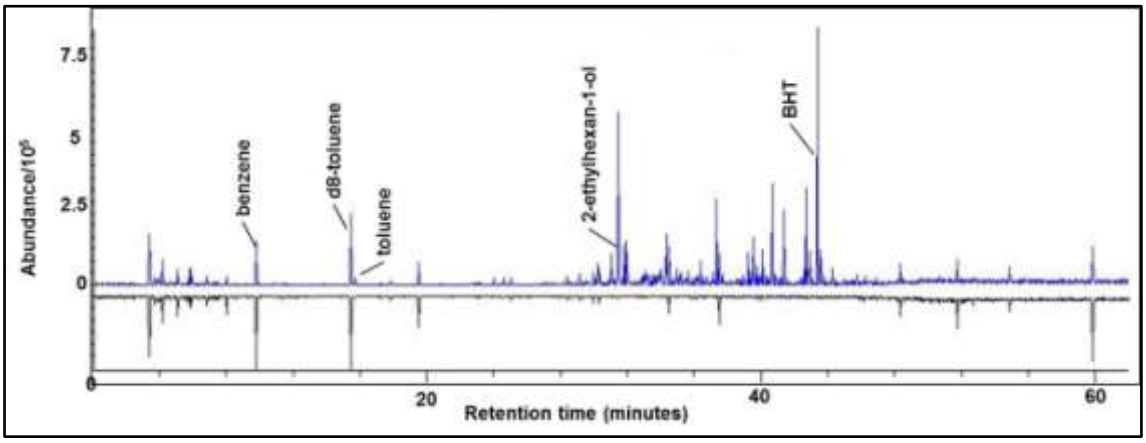

Figure 3-10 Chromatogram from Material A tested in the µ-CTE (blue trace) compared with a control (inverted black trace)

The chromatogram obtained on analysis of a Tenax TA tube used to sample air from the bag containing a piece of material A heated at 40 °C is shown in Figure 3-11 (blue trace). This figure also shows the chromatogram obtained by analysis of the first tube used to sample air from the control bag in the same experiment (inverted black trace). The chromatogram given by the material in the bag is very similar to that obtained from heating this material in the µ-CTE, but with relatively greater amounts of the more volatile compounds. This is to be expected as, with the bag sampling procedure, all compounds present will be trapped in the bag and transferred onto the tube during sampling, whereas using the µ-CTE, 20 minutes was allowed for equilibration at the temperature of the µ-CTE and in a flow of air before an air sample is taken. The most volatile components are therefore likely to be preferentially removed from the headspace during this equilibration period. Several of the peaks are also observed in the control chromatogram, these either being due to artefacts of the sorbent (e.g. benzene at RT 9.80 minutes) or contaminants from the bag (e.g. peak at RT 9.25 minutes tentatively identified as 2-methyl-1,3-dioxolane). Again a similar pattern of peaks was observed in the higher temperature test with greater absolute amounts and a shift towards greater relative amounts of the higher boiling compounds.

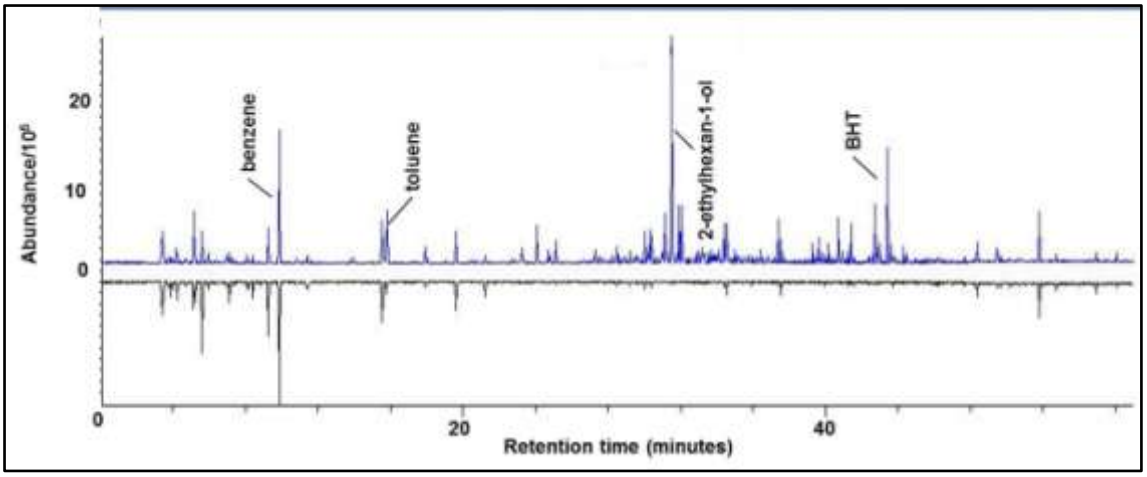

Figure 3-11 Chromatogram from Material A tested using bag sampling (blue trace) compared with control bag (inverted black trace)

The numbers of the compounds which had been analysed on the TD-100/GC/MSD system (at the time 100) and were present in the material and control chromatograms obtained from the µ-CTE and bag tests were determined and these are shown in Table 3-1. These demonstrate the presence of a greater number of peaks at the higher temperature tests than at 40 °C and in the bag test than using the µ-CTE. The greater number of compounds found from a control bag than from a control chamber in the µ-CTE is also highlighted.

Table 3-1 Number of target compounds emitted from Material A identified using different screening methods and temperatures

	µ-CTE, 40 °C	**µ-CTE, 65 °C**	**Bag, 40 °C**	**Bag, 60 °C**
Sample	17	27	31	40
Control	3	7	10	10

Amounts of three dominant compounds in the emissions from this material were determined for each of the µ-CTE and bag tests. It is not appropriate to make a direct quantitative comparison between these two types of test as one involves a dynamic headspace and the other is a static headspace, so results for the µ-CTE tests were expressed as specific emission rates (SERs) and results for the bag tests were expressed as ‘sampling bag values’. A sampling bag value for a compound is its concentration in

the test bag multiplied by the bag volume (as described in the procedure for this technique given in Appendix A.2).

Values obtained for the three selected compounds for each of these tests are shown in Figure 3-12. The shift towards greater amounts of the less volatile compounds from the higher temperature test is observed with the amount of 2-ethylhexan-1-ol released in the µ-CTE test at 65 °C being approximately three times the amount released at 40 °C, whereas the amount of BHT released at 65 °C was close to six times that released at 40 °C. Comparing the two techniques, a relatively greater amount of BHT than toluene was observed in the µ-CTE test than using the bag and at the higher temperature this difference increased.

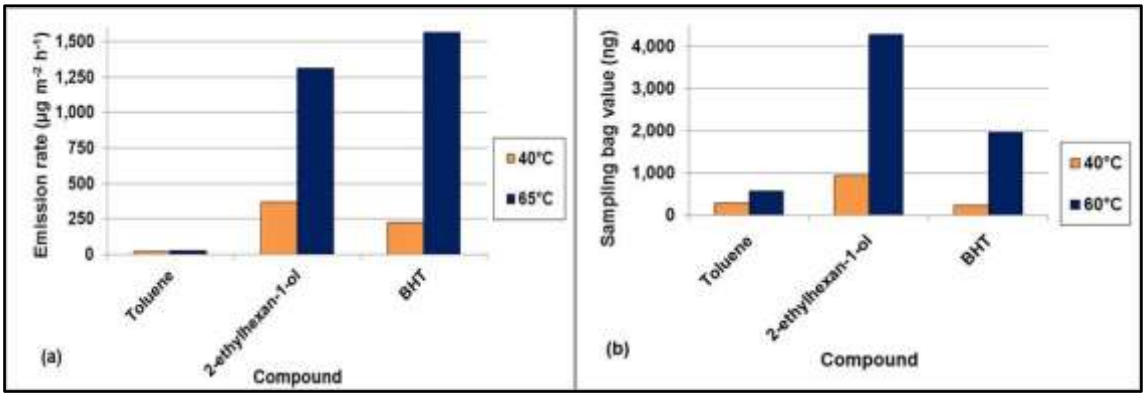

Figure 3-12 Amounts of three dominant VOCs released from Material A using (a) µ-CTE and (b) bag sampling

3.3.2.2 Material B (PVC)

Material B gave a different range of dominant peaks to those from Material A and a similar pattern of compounds using the two screening techniques (with the same difference in relative amounts of the more volatile compounds found). The chromatogram obtained from analysis of a Tenax TA tube used to sample from a bag containing a portion of this PVC material, heated at 40 °C is shown in Figure 3-13. The background peaks obtained from sampling from a control bag were similar to those found with Material A.

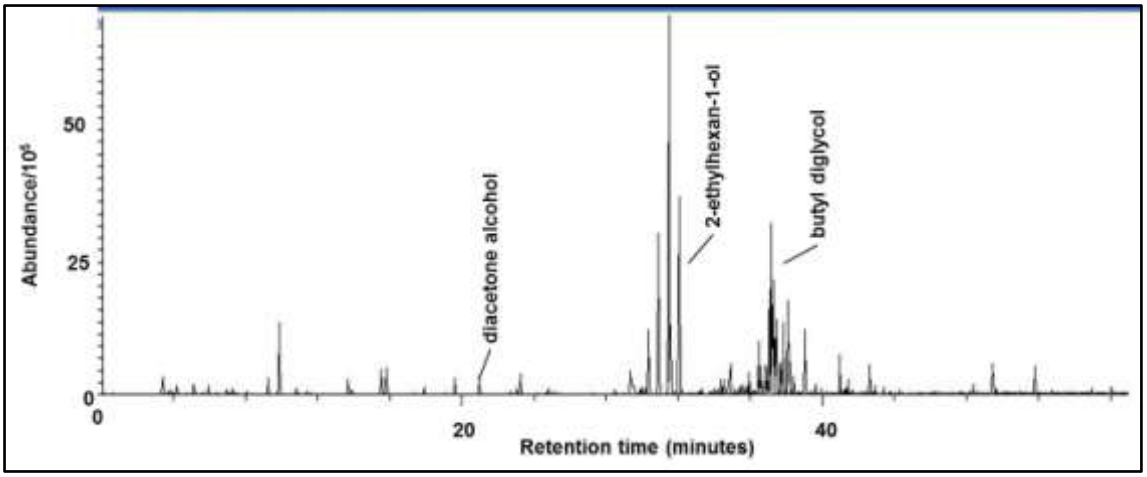

Figure 3-13 Chromatogram of emissions from material B tested using bag sampling

A comparison of the major compounds released from this material with those found on previous analysis, also using a μ-CTE, conducted elsewhere (Pharaoh, 2010) was undertaken and results obtained are shown in Table 3-2. For the present work, compounds which were not amongst those which have been determined using the current instrument and conditions (see Appendix F.2), were identified using the NIST library of mass spectra. These compounds are marked with an asterisk to show that the identification is tentative. The majority of compounds were observed during analyses by both laboratories, with only a small number being found in one chromatogram and not the other. Retention times found during the current work are longer than those obtained by Pharaoh; this is due to the use of a longer GC column (60 m), with a greater than typical film thickness (0.5 μm) and a slower GC oven ramp rate.

Amounts of three compounds observed in significant amounts from this material using the μ-CTE and bag tests are shown in Figure 3-14. No diacetone alcohol was observed in the μ-CTE test at 40 °C, whereas a small amount was seen in the higher temperature test. Amounts of 2-ethylhexan-1-ol and butyl diglycol were greater at the higher temperature. The bag tests gave some diacetone at both temperatures and greater amounts of the other two compounds from the higher temperature test. There is again seen to be a difference in the relative amounts of the different compounds observed between the two techniques.

Table 3-2 Comparison of major compounds found from material B using a µ-CTE by two different laboratories (previous work courtesy of Pharaoh, 2010)

Compound	Retention time (minutes)	
	Previous work	Present work
2-Butanone	6.05	7.25
Toluene	8.19	15.82
Diacetone alcohol	9.70	20.97
1-methyoxy-2-propylacetate	10.27	23.07 *
2-(2-Ethoxyethoy)ethanol	13.55	30.36
1-Propanol-2-(2-methoxy-1-methylethoxy)-	13.74	30.88 *
2-propanol, 1-(2-methoxypropoxy)	14.03	31.50 *
2-Ethylhexan-1-ol	Not identified	31.59
N-methyl-2-pyrrolidinone	14.46	32.07 *
2-Ethylhexanoic acid	15.70	34.94
Decamethylcyclopentasiloxane	Not identified	35.95
2-(2-Butoxyethoxy)ethanol (also known as butyl diglycol)	16.99	37.15
Cyclopropane-1-methyl-2-(methylpentyl)-	17.18	37.46 *
5-Methyl-1-heptanol	17.54	Not identified
Chlorododecane	20.31	42.65 *

* tentative identification using NIST library only

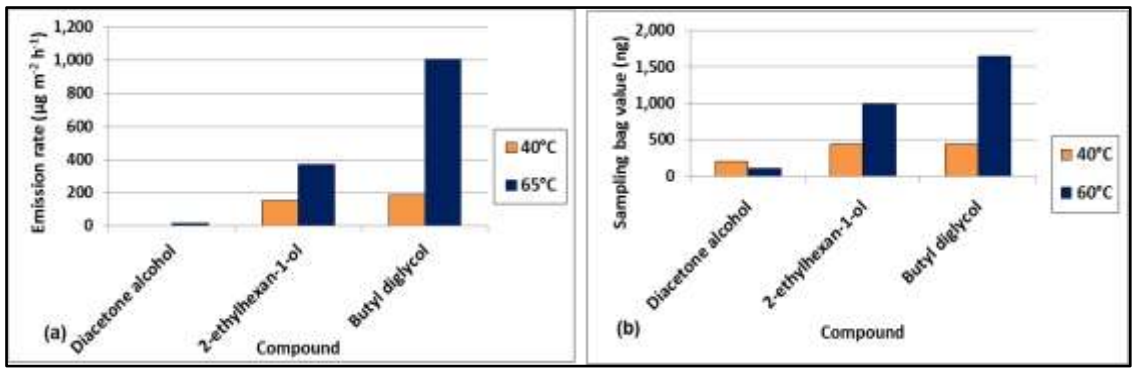

Figure 3-14 Amounts of three dominant VOCs released from Material B using (a) µ-CTE and (b) bag sampling

3.3.2.3 Material C (vinyl wallpaper)

The chromatogram obtained from analysis of a Tenax TA tube used to sample air from the bag containing the portion of material C heated at 40 °C is shown in Figure 3-15. This material was found to give one particularly dominant compound (2,2,4-trimethyl-pentanedioldiisobutyrate or TXIB) and much smaller amounts of several other compounds. In the higher temperature test and using the µ-CTE, the dominance of TXIB was even more apparent. The results obtained for TXIB and for two more volatile compounds in each of these tests are shown in Figure 3-16. Hexanal was only observed in the bag tests, whereas 2-ethylhexan-1-ol was found in relatively greater amounts in the bag tests than using the µ-CTE.

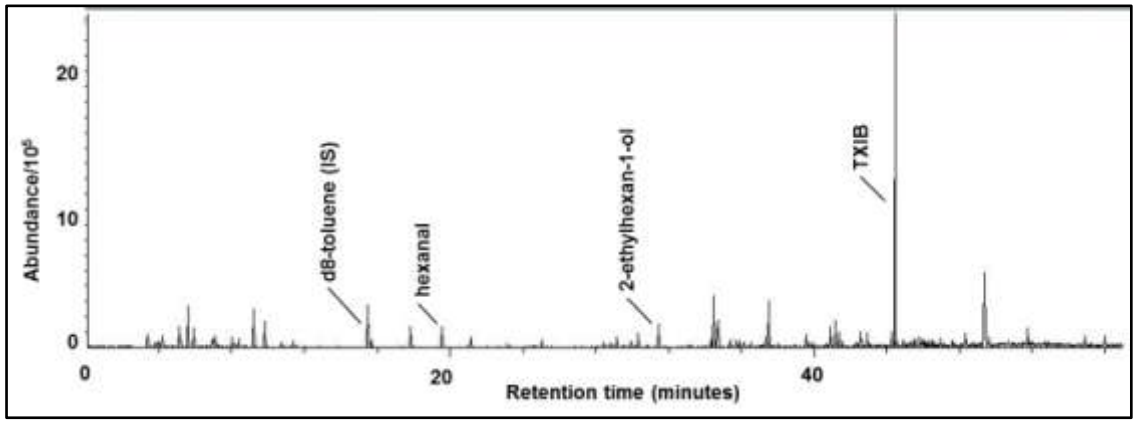

Figure 3-15 Chromatogram showing emissions from material C tested using bag sampling

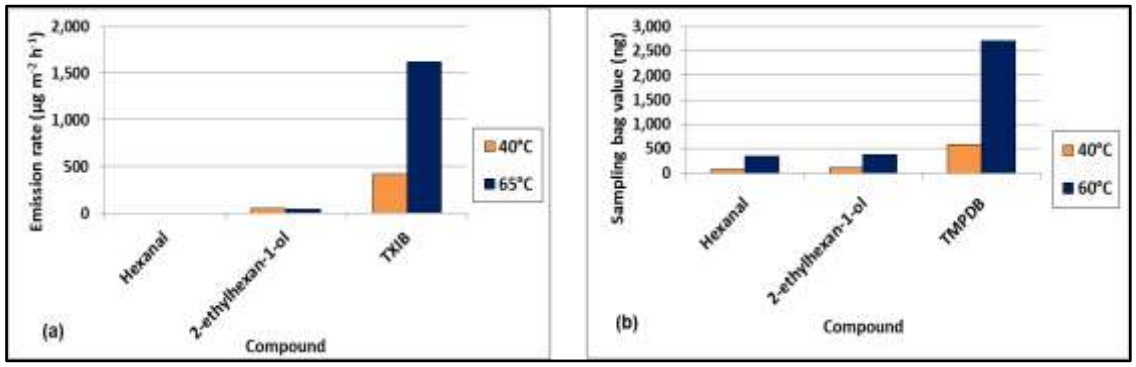

Figure 3-16 Amounts of three dominant VOCs released from Material C using (a) µ-CTE and (b) bag sampling

3.3.2.4 Material D (vinyl floor tile)

Material D gave three dominant compounds, toluene, cyclohexanone and 2-ethyl-hexan-1-ol at much greater amounts than for the other three materials. The chromatogram obtained from analysis of a Tenax TA tube used to sample air from the bag containing the portion of material D heated at 40 °C is shown in Figure 3-17. Amounts obtained in the bag tests were above the maximum of the calibration curves for the three compounds, so the resulting values are approximate. Figure 3-18 shows the results for these three compounds for both techniques. With the µ-CTE the same pattern of greater absolute amounts and greater relative amounts of higher boiling compounds at higher temperature is observed, whereas for the bag tests amounts obtained at the two temperatures are closer (though could be affected by the calibration issue).

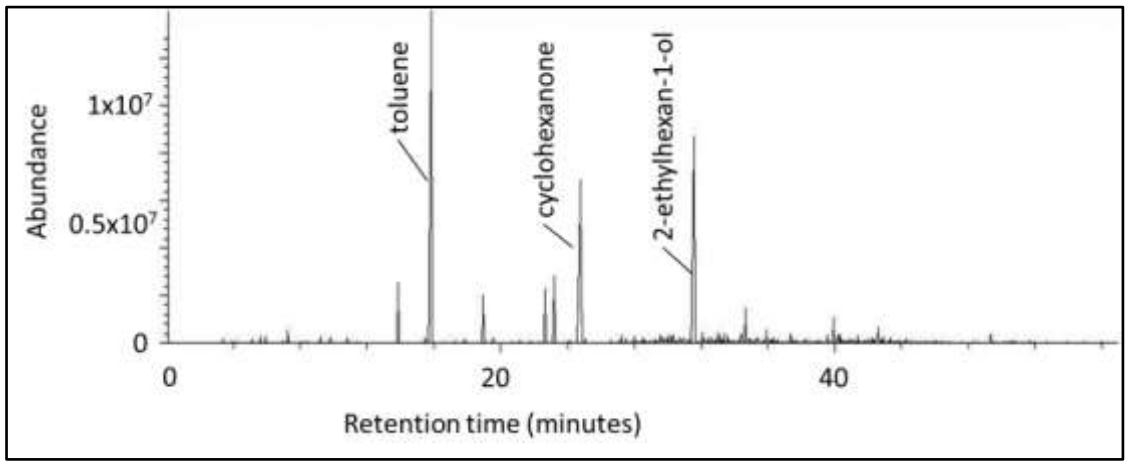

Figure 3-17 Chromatogram from material D tested using bag sampling

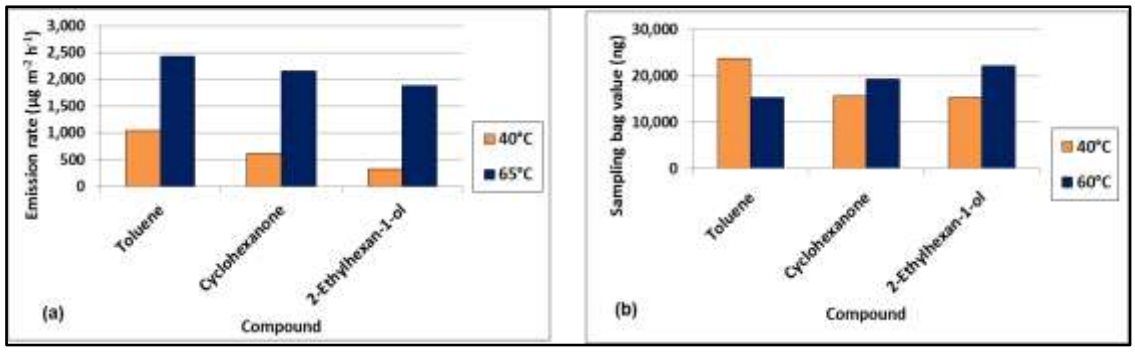

Figure 3-18 Amounts of three dominant VOCs released from Material D using (a) µ-CTE and (b) bag sampling

3.3.2.5 Comparison of bag and µ-CTE results

The results obtained from tests applying these two techniques to four materials which emitted different patterns of peaks suggest that the µ-CTE and the bag method can give broadly similar emission profiles for a particular material. The differences in the numbers of compounds detected and the relative amounts of compounds of different volatility observed using the µ-CTE and the sampling bag are likely to be due to the complementary approaches of the techniques. The dynamic nature of the µ-CTE process will allow preferential removal of volatile components from the material headspace during the equilibration period, whereas with the bag method all these compounds will be held in the bag until sampling is undertaken. Another difference between the two methods is that the bag method captures emissions from all surfaces of a material sample, whereas the µ-CTE is able to operate in either bulk or surface mode. When used in surface mode, as in this study, the µ-CTE can therefore be expected to give a more accurate representation of the likely emissions from a material which in use only has one surface exposed to the atmosphere.

Another issue with bag sampling is the presence of contaminants from the bag materials which may cause interference with compounds of interest. Ethylene glycol and 2-methyl-1,3-dioxolane have been observed in control bags in these experiments. The presence of trace levels of contaminants is difficult to eliminate from polymeric materials, other materials used for bag making also contain characteristic contaminant compounds, for example Tedlar bags release phenol and N,N-dimethylacetamide (Beauchamp et al., 2008). These contaminants are a problem if the same chemicals are emitted from the material under test, or else if they are large enough to obscure other compounds emitted from the material. The µ-CTE, on the other hand, while its cleanliness needs to be checked regularly, has been seen to be a source of little contamination.

The standard screening method for the determination of VOCs from vehicle interior parts and materials using a bag method (ISO 12219-2:2012), describes this method as offering a complementary approach to the micro-scale chamber and small chamber methods described in other standards in the same series. It states that bag sampling provides the automobile industry with a cost effective means of evaluating and

screening prototype materials during development and comparing emissions from products within a range (e.g. different colours or patterns). The technique does not appear to have been applied to the same extent to materials used in buildings. Gao et al., (2009) studied the emissions from a range of carpets using both a bag method and a 53 litre stainless steel chamber, though ambient temperature was used for these tests, rather than the elevated temperatures used in the present work. 2-ethylhexan-1-ol was found to be the dominant compound determined using both techniques. This compound was also amongst the largest peaks emitted from the carpet tested in the present study (and was also observed from the other materials studied). It is often found in indoor air due to hydrolysis of phthalate esters contained in PVC materials (Sakai et al., 2009). Also in common with the present study, the study by Gao et al. (2009) found consistently greater numbers of compounds from the bag tests than from the chamber tests. In both studies the extra compounds tended to be of high volatility. Use of the bag method could therefore result in concern regarding the presence of some compounds which in dynamic chamber tests (or in situ within a building) are rapidly depleted by ventilation to negligible levels.

As might have been expected, the higher temperature tests, as used in tests of VOCs emitted from car interior materials, resulted in greater amounts of VOCs being released, particularly of the less volatile compounds. This can help to reduce the time required for a screening test to be undertaken and can also demonstrate the potential emissions from a material in use which has been subjected to heating, for example through exposure to sunlight or proximity of a heating pipe. If wishing to use the screening tests to predict the findings of a reference emission test, however, too high a temperature may result in the emission of compounds which would not be observed from reference emission tests. The ASTM screening method for emissions from materials (D7706-11), which was published during the course of this project, recommends using 40 °C as the initial temperature, then investigating temperatures between 30 °C and 60 °C, and comparing the results with those obtained from a reference emission test. In the following section results obtained from testing a range of wall covering materials for different times and at different temperatures using the µ-CTE will be compared with those obtained from use of a FLEC.

3.3.3 Comparison of µ-CTE and FLEC tests

3.3.3.1 Wall covering 1

Wall covering 1 tested in the µ-CTE at 23 °C gave one dominant compound which was identified as TXIB (2,2,4-trimethylpentanedioldiisobutyrate). The chromatogram also included a range of aliphatic hydrocarbons of carbon chain length 10-12 and amongst this group a peak which was identified as 2-ethylhexanoic acid (2-EHA). This material tested in the µ-CTE at 40 °C showed the same pattern of peaks at greater intensities. A chromatogram from the 40 °C test on this material is shown in Figure 3-19. TXIB is used as a processing aid in the manufacturing of plastisols. This compound has a relatively high boiling point (280 °C) and elutes just after n-hexadecane, so it is at the cross-over point between VOCs and SVOCs (semi-volatile organic compounds), whereas the other compounds observed in the chromatogram are all VOCs. 2-EHA has been previously observed in the emissions from two PVC wall coverings (Schripp et al., 2007).

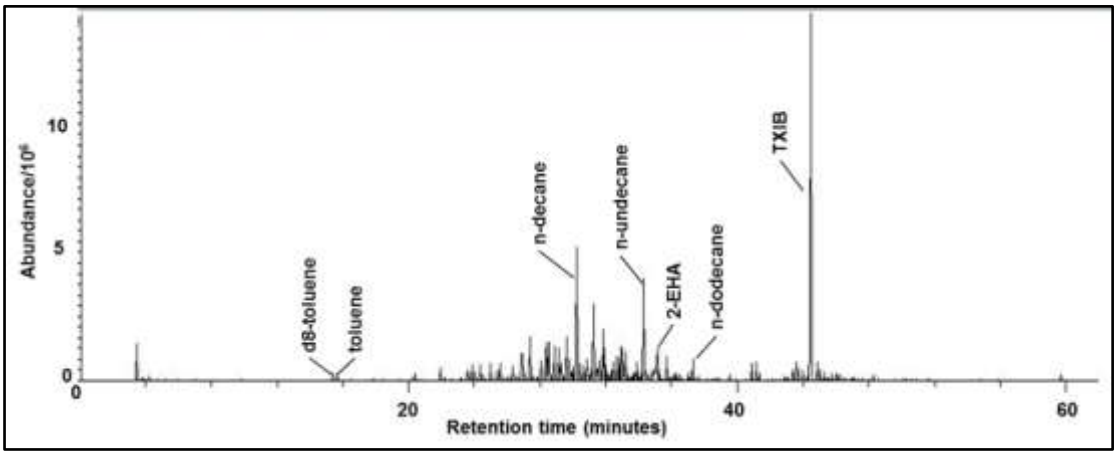

Figure 3-19 Chromatogram from sample of wall covering 1 tested in the µ-CTE at 40 °C

Mean emission rates obtained for the dominant compounds observed in the chromatograms and for TVOCs are shown in Table 3-3. These values have been corrected for amounts of VOCs found on blank tubes (see Appendix B.1). TXIB has not been included in the TVOC values. For the 40 °C test, TXIB and n-decane were above the linear range of their calibration curves, so it is likely that their rates are underestimated. Comparing the emission rates immediately after the samples were

placed in the µ-CTE with those after 15 minutes shows a reduction in levels of the more volatile compounds, whereas similar amounts of the less volatile compounds were observed for both sampling periods. Comparison of emission rates obtained at 23 °C with those found at 40 °C shows rates some 2-3 times higher at the higher temperature.

The % relative standard deviation (RSD) for sets of replicate samples ranged between 7.4 % for TVOCs at 23 °C to 37.5 % for toluene at 40 °C. The lower end of this range is a typical value for replicate analyses on the TD-100/GC/MSD system, so it is likely that inhomogeneity in the replicate samples are contributing to the variation in emission rates for some of these compounds. As this wall covering material is patterned and the samples were cut from the sheet randomly the different parts of the design might have resulted in different amounts of VOCs being released. This is demonstrated by the six portions of material tested in the µ-CTE at 40 °C (Plate 3-2).

Table 3-3 Dominant compounds emitted from wall covering 1 tested in the µ-CTE

Compound	Emission rate (µg m^{-2} h^{-1})			
	µ-CTE test, 23 °C Mean (n=6) (% RSD)		µ-CTE test, 40 °C Mean (n=6) (% RSD)	
	1st tube	2nd tube	1st tube	2nd tube
Toluene	152 (14.4 %)	90.6 (21.0 %)	299 (26.8 %)	112 (37.5 %)
n-Decane	2,140 (11.5 %)	1,520 (12.7 %)	4,200 (15.5 %) *	2,660 (18.3 %) *
n-Undecane	1,020 (13.7 %)	794 (13.9 %)	2,370 (16.7 %)	1,630 (15.8 %)
2-EHA [1]	404 (22.7 %)	488 (19.6 %)	2,500 (22.6 %)	2,610 (21.4 %)
n-Dodecane	95.8 (11.4 %)	78.6 (13.1 %)	275 (16.2 %)	202 (15.6 %)
TXIB [2]	3,160 (12.1 %)	3,350 (17.2 %)	5,580 (17.4 %) *	5,800 (13.3 %) *
TVOCs	13,000 (12.9 %)	9,700 (7.4 %)	43,000 (14.7 %)	25,100 (18.0 %)

[1] 2-EHA = 2-ethylhexanoic acid; [2] TXIB – 2,2,4-Trimethylpentanedioldiisobutyrate

* responses above top of calibration curve so amount may be underestimated

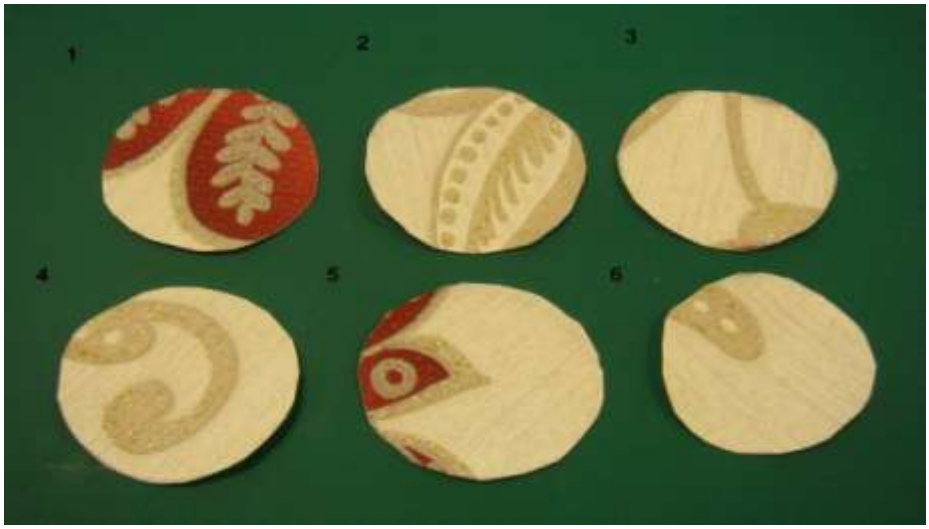

Plate 3-2 Discs of wall covering 1 tested in the µ-CTE at 40 °C

A chromatogram from a sample of wall covering 1 which had been placed under the FLEC one hour earlier is shown in Figure 3-20. This shows a very similar pattern of dominant peaks and relative proportions as found in the µ-CTE test of this material, i.e. a group of aliphatic hydrocarbons and a high emission of TXIB. As the experiment continued the emission rates declined. The emission rate profile for TVOCs over the first three days of the test showed an initial sharp decline followed by a levelling out. This is shown in Figure 3-21 in which each point is the mean obtained from two tubes used to sample from the FLEC. These values have been corrected for amounts of VOCs found on control tubes (see Appendix B.2).

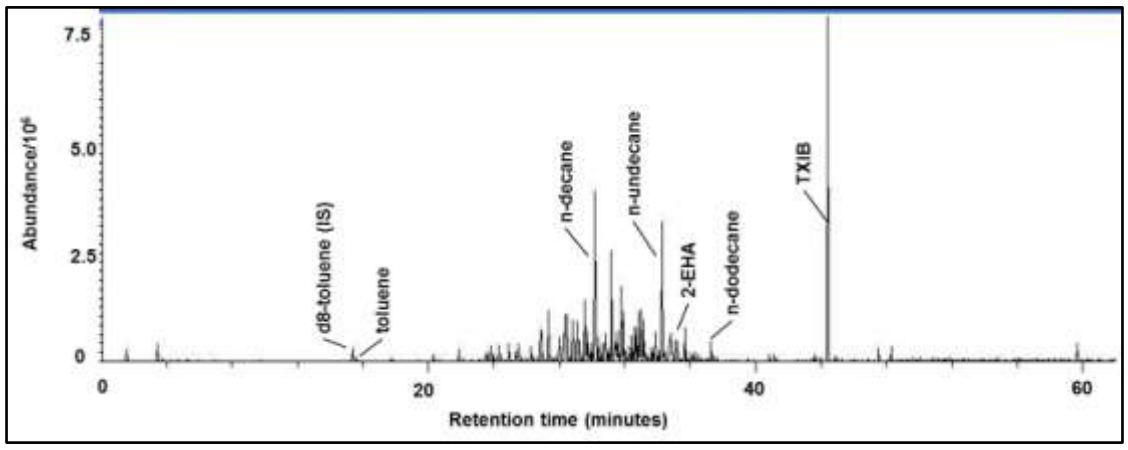

Figure 3-20 Chromatogram from sample of wall covering 1 one hour after placed in the FLEC

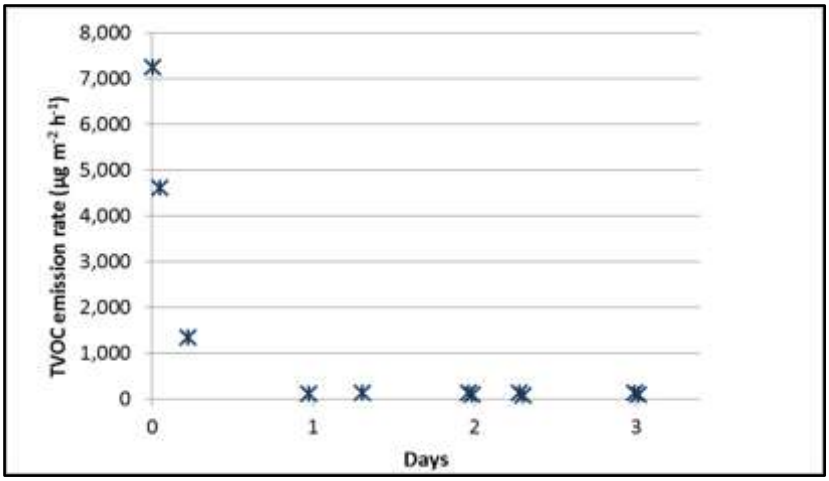

Figure 3-21 Change in TVOC emission rate from wall covering 1 with time under the FLEC

A study of the emission profiles of different compounds shows that the more volatile compounds declined faster than those less volatile. The emission profile for n-undecane and TXIB are shown in Figure 3-22. The n-undecane has declined to a low level after 1 day, whereas TXIB shows a rise in emission rate over this period followed by a stable rate. At the 28 day sampling, detectable levels of TXIB and 2-ethylhexanoic acid only are observed.

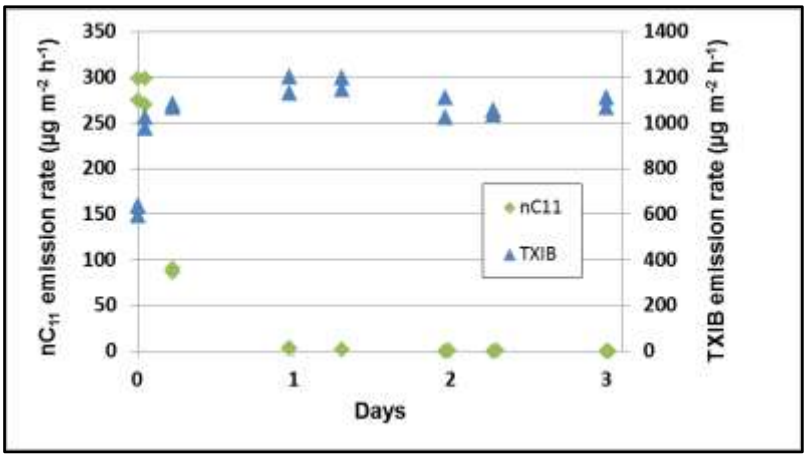

Figure 3-22 Emission rates of n-undecane and TXIB from wall covering 1 tested using the FLEC

3.3.3.2 Wall covering 2

Wall covering 2 gave a similar emission profile to that obtained with wall covering 1, with TXIB dominating the chromatogram and smaller amounts of a group of aliphatic hydrocarbons. Figure 3-23 shows chromatograms obtained from two of the samples of wall covering 2 tested in the µ-CTE at 40 °C. TXIB is seen to occur in a very similar amount in the two samples, amounts of the aliphatic hydrocarbons, however, vary significantly between the two samples.

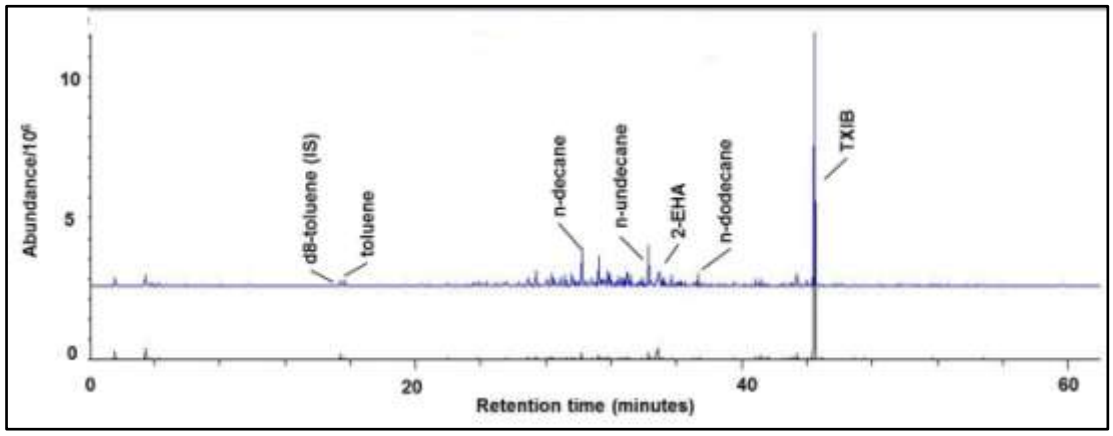

Figure 3-23 Chromatograms from two samples of wall covering 2 tested in the µ-CTE at 40 °C

Relative standard deviations of the emission rates for this material, Table 3-4, range from 3 % for TXIB at 23 °C to 96 % for TVOCs at 40 °C. This variability is again thought to be due to the pattern on the material, the highest values were obtained from portions of the material from the 40 °C test which had been placed in chambers 3 and 6 which do appear quite distinct from the remaining samples (Plate 3-3). The variability between samples at 23 °C was lower than at 40 °C, which may be explained by the observation that all the samples tested at the lower temperature had been taken (without deliberate selection) from the lighter coloured part of the pattern.

Table 3-4 Dominant compounds emitted from wall covering 2 tested in the µ-CTE

Compound	Emission rate (µg m^{-2} h^{-1})			
	µ-CTE test, 23 °C Mean (n=6) (% RSD)		µ-CTE test, 40 °C Mean (n=6) (% RSD)	
	1st tube	2nd tube	1st tube	2nd tube
Toluene	109 (9.5 %)	70.6 (15.2 %)	189 (56.4 %)	87.7 (48.1 %)
n-Decane	434 (11.9 %)	311 (12.4 %)	778 (75.1 %)	443 (74.7 %)
n-Undecane	264 (11.8 %)	203 (11.2 %)	550 (81.0 %)	352 (86.4 %)
2-EHA	158 (8.4 %)	179 (6.8 %)	862 (53.7 %)	849 (54.0 %)
n-Dodecane	34.6 (12.3 %)	28.8 (9.3 %)	105 (68.9 %)	72.6 (79.7 %)
TXIB	942 (3.3 %)	1,050 (4.5 %)	4,400 (20.0 %) *	4,440 (19.7 %) *
TVOCs	4,050 (15.8 %)	2,420 (19.8 %)	8,250 (90.4 %)	4,920 (96.1 %)

* responses above top of calibration curve so amount may be underestimated

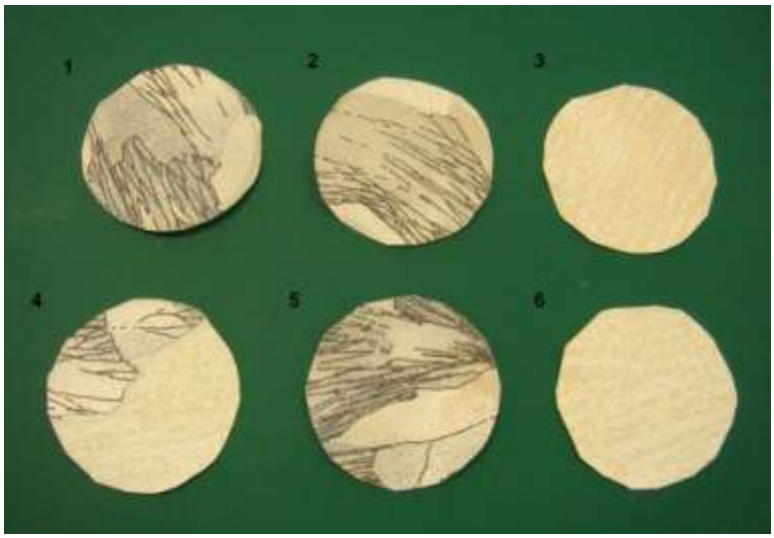

Plate 3-3 Discs of wall covering 2 tested in the µ-CTE at 40 °C

The 40 °C test with this material again showed higher amounts than found at 23 °C, with a tendency for a bigger difference for the less volatile compounds. This test also shows the same finding of a reduction in the amounts of the more volatile compounds from the first to the second air sampling period, whereas the less volatile compounds are more equivalent. In comparison with wall covering 1, this material is found to release lower amounts of all compounds, resulting in TVOC values which were 3-5 times lower than for wall covering 1.

Figure 3-24 shows the chromatogram obtained one hour after the start of the test of wall covering 2 in the FLEC. The dominant compounds observed and the relative proportions are as seen using the µ-CTE test of this material, i.e. as for wall covering 1, but with relatively lower amounts of hydrocarbons. The TVOC emission rate for this material using the FLEC was initially about one half that of wall covering 1 (around 3,500 µg m^{-2} h^{-1}) and it followed a similar pattern, declining to 1,000 µg m^{-2} h^{-1} after four hours and to 100 µg m^{-2} h^{-1} after 1 day. As with wall covering 1, the more volatile compounds showed a faster drop off in emissions than the less volatile compounds.

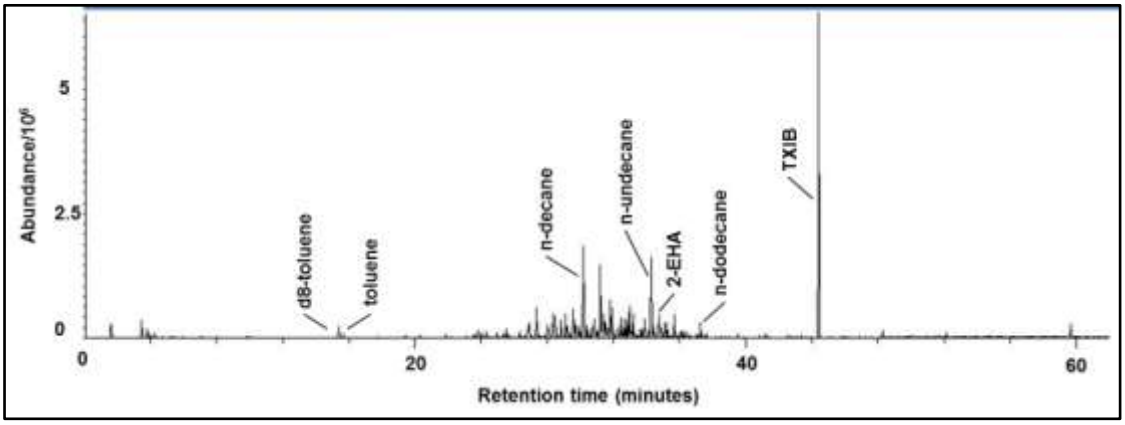

Figure 3-24 Chromatogram from sample of wall covering 2 one hour after placed in the FLEC

Figure 3-25 shows the emission profile of n-decane and TXIB from this material tested in the FLEC. Each point represents an individual air sample as sequential sampling was undertaken during this test. While n-decane declines to a non-detectable level after 1 day, the emission of TXIB increases during the first day to a rate of about 400 µg m^{-2} h^{-1}, which is about one third of that released from wall covering 1. After 28 days the material was still emitting detectable amounts of 2-ethylhexanoic acid and TXIB.

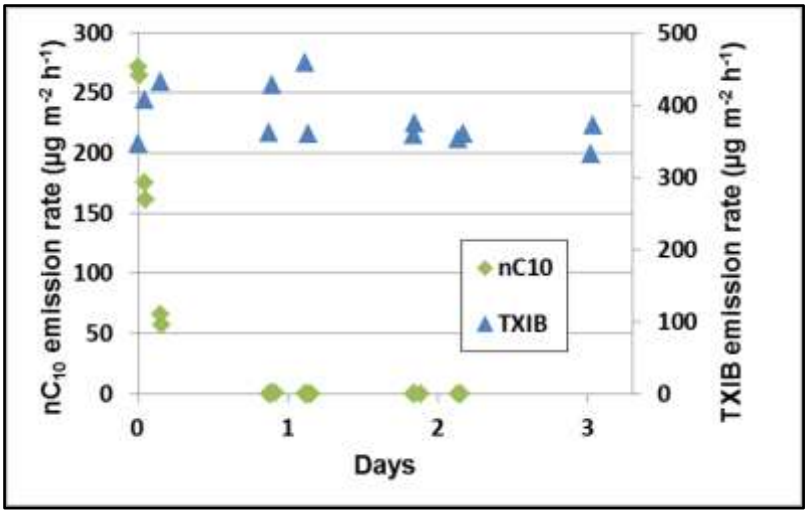

Figure 3-25 Emission rates for n-decane and TXIB from wall covering 2 tested using the FLEC

3.3.3.3 Wall covering 3

Chromatograms from two of the samples of wall covering 3 tested in the µ-CTE at 40 °C are shown in Figure 3-26. In these chromatograms the levels of VOCs are significantly lower than for wall coverings 1 and 2 and the pattern of peaks is different. One particular pair of peaks is seen to vary significantly between the samples. This compound, which is known as Texanol (2,2,4-trimethylpentanediol monoisobutyrate), and occurs as a mixture of two isomers, is mainly used as a coalescing agent for latex based paints (Lin and Corsi, 2007). Toluene and TXIB are also present in the emissions from this material, at much lower levels than found for the first two wall coverings, but the group of aliphatic hydrocarbons are not seen. The chromatogram also shows the presence of small amounts of a group of glycol ethers including 2-butoxyethanol (2-BE). The variation in emissions between replicates can again be explained by the choice of sections of the material to sample. Plate 3-4 shows the samples tested at 40 °C, the highest Texanol levels were found from those placed in chambers 2 and 3 which are seen to display a distinct ridged pattern not observed in the other samples.

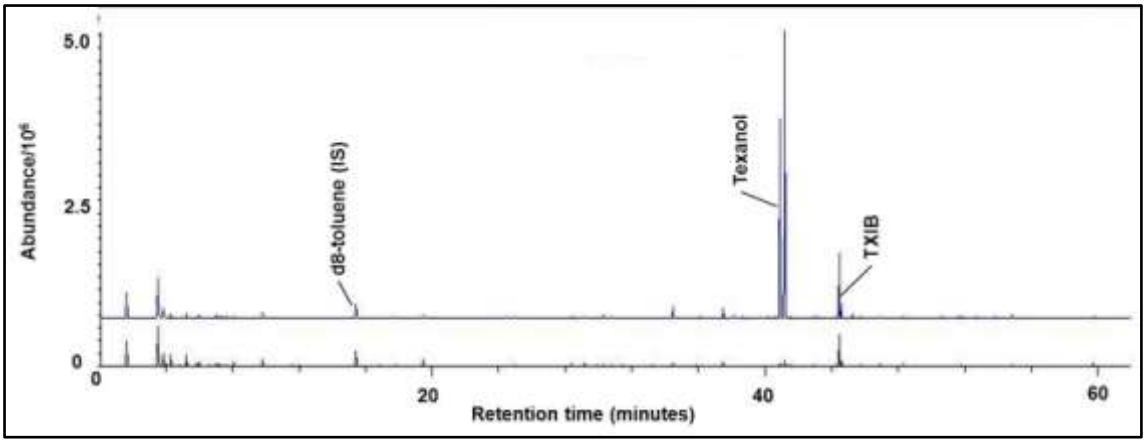

Figure 3-26 Chromatograms from two samples of wall covering 3 tested in the µ-CTE at 40 °C

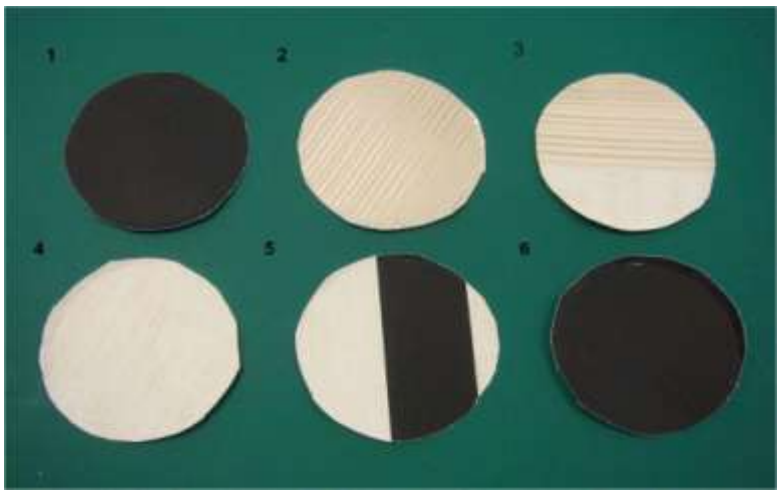

Plate 3-4 Discs of wall covering 3 tested in the µ-CTE at 40 °C

Emission rates for the dominant compounds and TVOCs from the two µ-CTE tests of this material conducted at different temperatures are shown in Table 3-5. The values obtained at 40 °C were higher than found at 23 °C, with the exception of toluene for which just detectable results were obtained only for the immediate sampling period (1st tube). For the 40 °C test, the run was extended to investigate whether this gave improved comparability with results from the FLEC. This involved continuing the heat and flow of air to the µ-CTE and taking a third set of air samples two hours from the start of the test and a fourth set of air samples five hours from the start. For these, Texanol was present in some of the replicates, TXIB was present at a low level in all tubes, and no other VOCs were seen.

Table 3-5 Dominant compounds emitted from wall covering 3 tested in the µ-CTE

Compound	Emission rate (µg m^{-2} h^{-1})					
	µ-CTE test, 23 °C Mean (% RSD)		µ-CTE test, 40 °C Mean (n=6) (% RSD)			
	1st tube (n=5)[1]	2nd tube (n=4)[1]	1st tube	2nd tube	3rd tube	4th tube
Toluene	10.2 (9.1 %)	Not detected	4.6 (34.5 %)	Not detected	Not detected	Not detected
2-Butoxy-ethanol (2-BE)	56.7 (13.7 %)	Not detected	84.0 (39.4 %)	44.5 (14.5 %)	Not detected	Not detected
Texanol [2]	459 (71.0 %)	341 (99.7 %)	967 (144 %)	595 (142 %)	184 (111 %)	89.7 [3] (37.4 %)
TXIB	82.5 (235 %)	74.6 (44.3 %)	194 (49 %)	135 (41.4 %)	67.1 (28.8 %)	26.6 (8.5 %)
TVOCs	854 (62.5 %)	457 (111 %)	1,380 (138 %)	828 (148 %)	373 [3] (92.0 %)	54.1 [4] (34.1 %)

[1] Missing results due to analysis failure; [2] 2,2,4-trimethylpentanediolmonoisobutyrate (sum of isomers); [3] detectable in only 3 samples; [4] detectable in only 2 samples

The chromatogram obtained from testing a sample of wall covering 3 one hour after it had been placed in the FLEC (Figure 3-27) shows the dominant peak to be 2-BE. Texanol, TXIB and the other glycol ethers found from sampling using the µ-CTE are also observed. The amount of Texanol is lower than seen in some of the replicates with the µ-CTE and is again likely to result from the portion of the material selected for testing. The discs of these materials which were tested in the FLEC are shown in Plate 3-5; that for wall covering 3 shows very little of the part of the pattern which gave the highest Texanol emissions in the µ-CTE (i.e. the ridge pattern). The TVOC emission rate for this material was found to be around 200 µg m^{-2} h^{-1} after 1 hour and shows a similar decrease with time as the other materials, reaching 15 µg m^{-2} h^{-1} after 1 day.

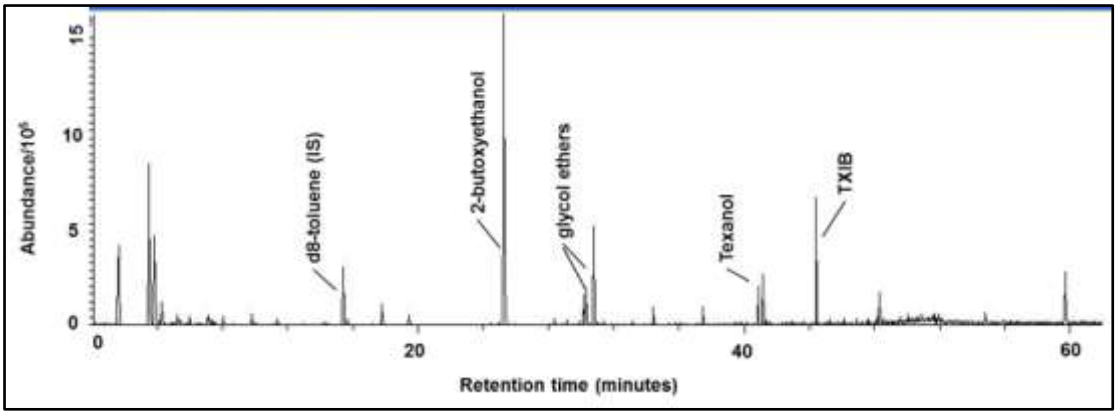

Figure 3-27 Chromatogram from sample of wall covering 3 one hour after placed in the FLEC

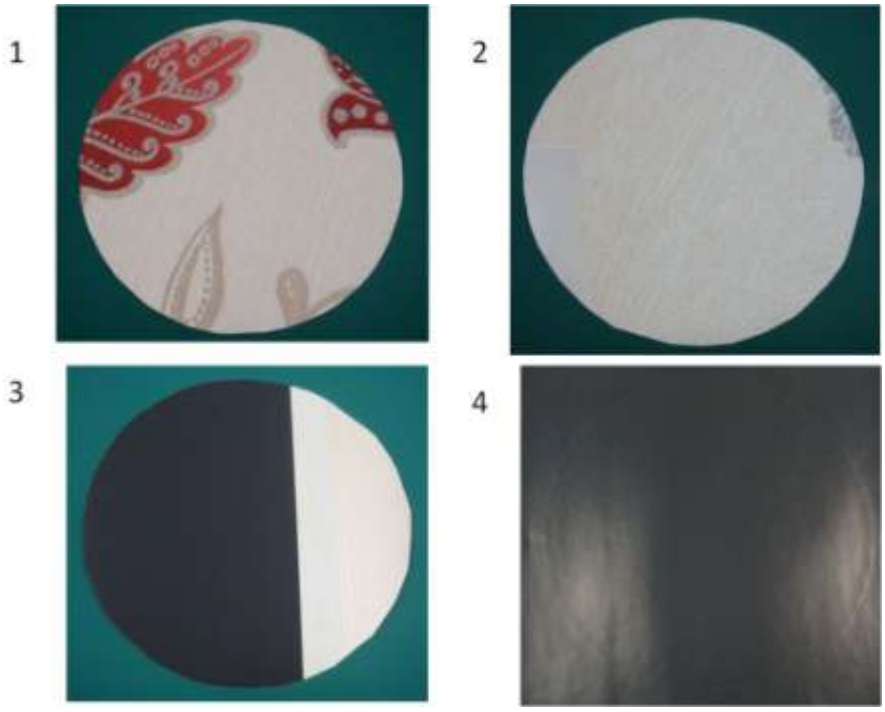

Plate 3-5 Portions of the four wall covering materials tested using the FLEC

Emission profiles for 2-BE and TXIB from this material (Figure 3-28) show a sharp drop off for 2-BE, while TXIB first increases then gradually decreases. After three days no TVOC emission was detectable from this material, but TXIB was still being emitted at a low level and this was also the case at 28 days.

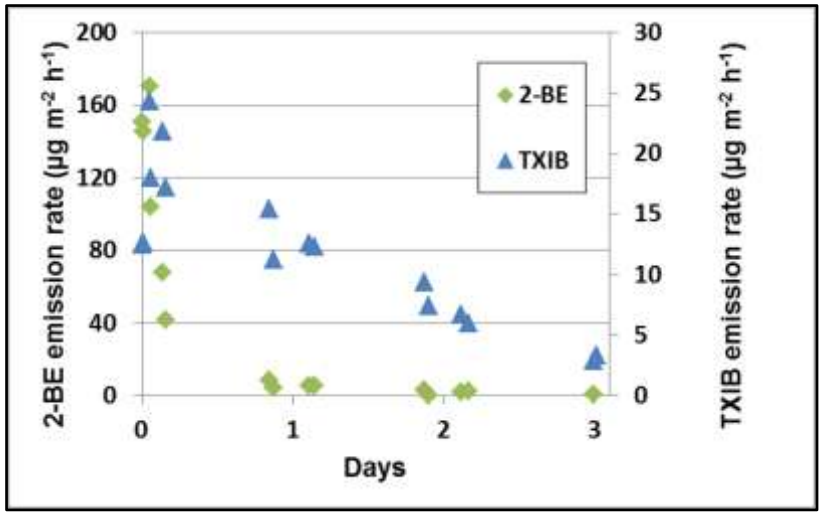

Figure 3-28 Emission profile for 2-butoxyethanol (2-BE) and TXIB from wall covering 3 tested using the FLEC

3.3.3.4 Wall covering 4

No detectable amounts of any VOCs were found from any of the chambers in the test of samples of wall covering 4 in the µ-CTE at 23 °C. In the 40 °C test of this material (Figure 3-29) the same compounds are found as for wall coverings 1 and 2, but at much lower levels. Table 3-6 shows the resulting emission rates. This material does not have a pattern (it is plain black) and this could explain the generally lower variability obtained for replicates. A reduction in emission is again observed between the first and second sampling period for all compounds other than 2-EHA and TXIB.

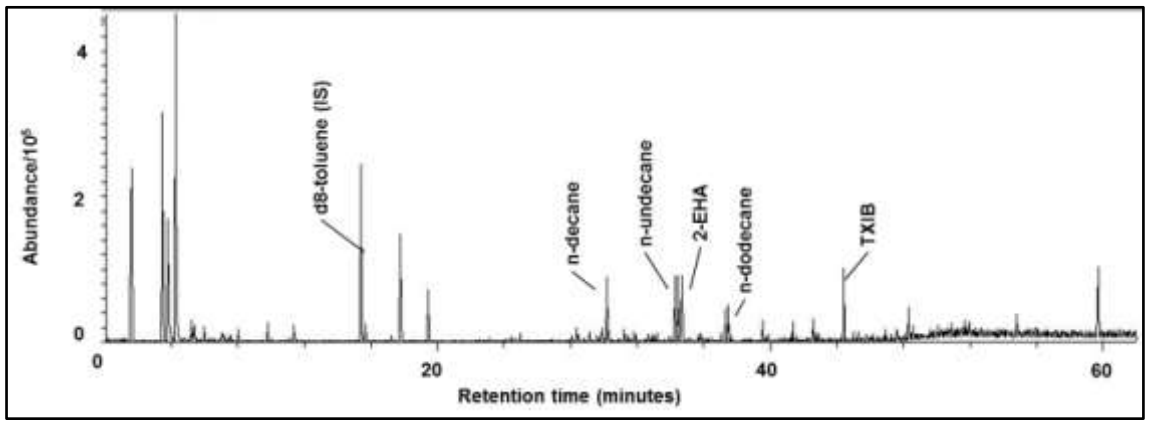

Figure 3-29 Chromatogram from sample of wall covering 4 tested in the µ-CTE at 40 °C

Table 3-6 Dominant compounds emitted from wall covering 4 tested in the µ-CTE

Compound	Emission rate (µg m^{-2} h^{-1})			
	µ-CTE test, 23 °C Mean (n=6) (% RSD)		µ-CTE test, 40 °C Mean (n=6) (% RSD)	
	1st tube	2nd tube	1st tube	2nd tube
Toluene	Not detected	Not detected	30.1 (10.5 %)	15.1 (12.3 %)
n-Decane	Not detected	Not detected	55.5 (8.9 %)	36.0 (7.1 %)
n-Undecane	Not detected	Not detected	39.9 (11.5 %)	27.1 (8.7 %)
2-EHA	Not detected	Not detected	162 (5.4 %)	173 (4.0 %)
n-Dodecane	Not detected	Not detected	11.7 (12.1 %)	8.6 (8.2 %)
TXIB	Not detected	Not detected	17.8 (15.7 %)	20.5 (13.1 %)
TVOCs	Not detected	Not detected	254 (17.2 %)	125 (17.4 %)

The chromatogram obtained from the portion of wall covering 4 one hour after placed under the FLEC is shown in Figure 3-30. As with the µ-CTE test of this material, dominant compounds were identified as toluene, n-decane, n-undecane and TXIB, in substantially lower amounts than found for the other materials. The TVOC emission rate after one hour was 140 µg m^{-2} h^{-1} and this had reduced to 20 µg m^{-2} h^{-1} after one day. The emission profile for toluene and TXIB is shown in Figure 3-31. Each point is the mean of duplicate samples. After three days only trace levels of 2-EHA and TXIB were detected, so it was decided not to continue this test until 28 days.

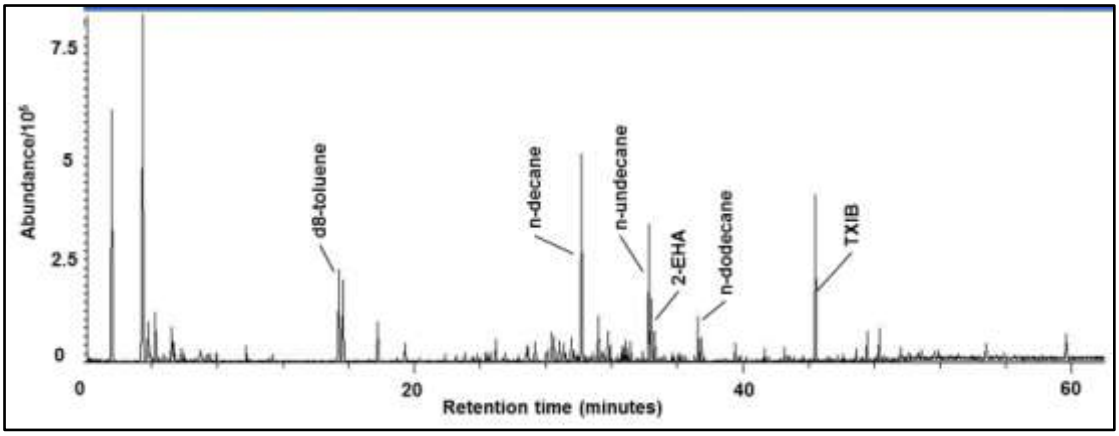

Figure 3-30 Chromatogram from sample of wall covering 4 one hour after placed in the FLEC

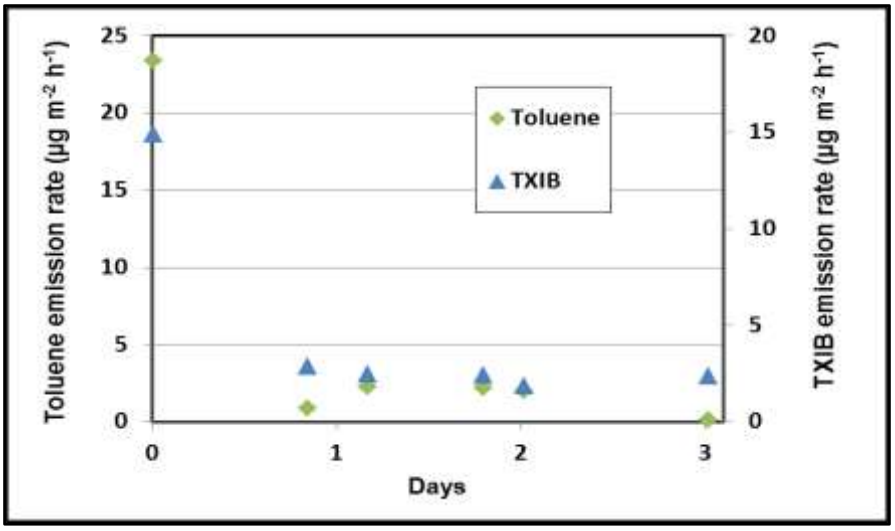

Figure 3-31 Emission profile for toluene and TXIB from wall covering 4 tested using the FLEC

3.3.3.5 Repeat of wall covering 1

In order to investigate further the comparability of results achievable using the µ-CTE and the FLEC, a second test of wall covering 1 was undertaken in the µ-CTE using a temperature of 40 °C. For this test, three sets of tubes were used to take consecutive 15 minute air samples from the µ-CTE, following an equilibration period of 15 minutes after placement of the material samples in the chambers. Further 15 minute sampling periods were started 75 and 105 minutes after the start of the test. During the analysis of these tubes the split flow was re-collected for re-analysis with a higher split ratio in order to provide more accurate emission rate values for TXIB, for which the results for this material had previously been above the top of the calibration range. The same pattern of peaks was observed as in the previous analysis of this material. Emission rates obtained for n-undecane and TXIB are given in Figure 3-32. These are the mean values obtained from the six replicate portions of the material sampled. As expected, the emission rate of TXIB was fairly stable over these five sampling periods, actually showing a moderate increase, while that of other compounds, including n-undecane, declined sharply. N-undecane and the other aliphatic hydrocarbons, which had been observed as dominant peaks in the early samples, were still detectable in the last sample taken from this material.

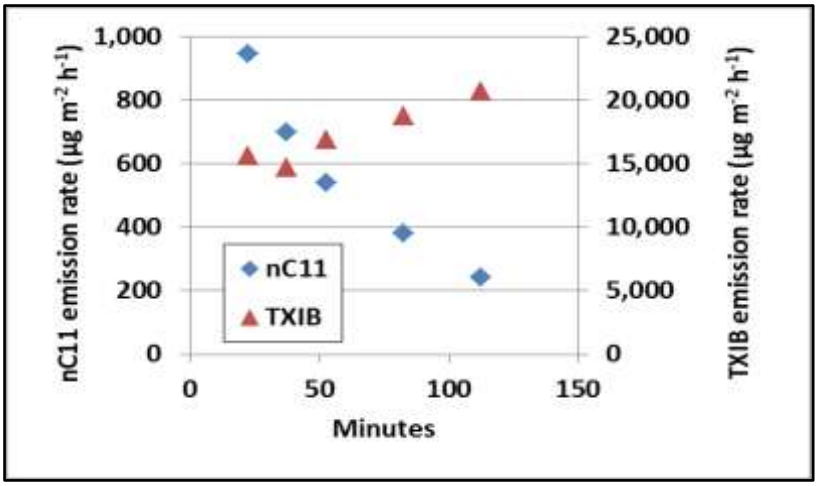

Figure 3-32 Emission profile for n-undecane (nC11) and TXIB from repeat test of wall covering 1 using the µ-CTE

3.3.3.6 Comparison of µ-CTE and FLEC results for wall covering materials

The samples taken early in the µ-CTE and FLEC tests of these materials showed the same dominant compounds and pattern of peaks for each material using the two techniques. At the testing times required by many of the labelling schemes (3 and 28 days) the FLEC tests showed that only the less volatile compounds were still being emitted from these materials. The aim of this work is to investigate whether a set of conditions for the µ-CTE test can be identified which can be used to predict the emission after a longer period of time from the FLEC. Using an elevated temperature for the µ-CTE test, it is not expected to obtain direct quantitative comparability between the two techniques. Table 3-7 shows the emission rates for TVOCs and individual compounds obtained for these four materials after 3 and 28 days using the FLEC. The emission rates for these compounds found in the 40 °C test with the µ-CTE after 15 minutes (and the tests after a longer time for wall coverings 1 and 3) are also included in the table. While the values obtained for the µ-CTE are higher, the materials giving the highest values (wall covering 1 and 2) tend to be the same with both techniques, suggesting that a quick test using the µ-CTE can predict which of the materials may have continuing high emissions.

Table 3-7 Comparison of emission rates for four wall covering materials obtained with the µ-CTE and the FLEC

Compound	Emission rate (µg m^{-2} h^{-1})											
	Wall covering 1				Wall covering 2			Wall covering 3			Wall covering 4 [1]	
	µ-CTE 15-30 min	µ-CTE repeat 15-30 min (2 hr) [2]	FLEC 3 days	FLEC 28 days	µ-CTE 15-30 min	FLEC 3 days	FLEC 28 days	µ-CTE 15-30 min (5 hr) [2]	FLEC 3 days	FLEC 28 days	µ-CTE 15-30 min	FLEC 3 days
2-EHA	2,610	2,330 (1,950)	185	78.7	849	77.0	47.1	Not detected	Not detected	Not detected	173	18.8
Texanol	285	264 (290)	16.7	Not detected	122	3.6	Not detected	595 (90) [3]	3.2	Not detected	Not detected	Not detected
TXIB	5,800 [5]	15,600 (20,700)	1,090	101	4,440 [5]	353	97.6	135 (27)	3.1	2.3	20	2.3
TVOCs	25,100	11,900 (4,530)	85.6	20.5	4,920	67.2	37.2	572 (54) [4]	Not detected	Not detected	125	10.8

[1] no test undertaken at 28 days for this material; [2] air sample taken after material had been exposed in the µ-CTE for an extended period,

[3] only seen in three of the samples; [4] only seen in two of the samples; [5] response above top of calibration curve so amount may be underestimated

One way of demonstrating the comparability between the two techniques might be to see how similarly they rank the products according to the amount of emissions. These rankings (in order of decreasing emission rate) are shown in Table 3-8. Other than for Texanol, for which inhomogeneity in the material was thought to have resulted in greater amounts being emitted from some of the replicate samples tested in the µ-CTE than from the portion tested in the FLEC, both tests consistently rank wall coverings 1 and 2 as higher emitting materials than wall coverings 3 and 4. These results therefore also highlight one issue in sampling with small portions of material, which is the importance of selection of the sample from the material to be tested. This has been found to be a potential issue for both the µ-CTE and the FLEC.

Table 3-8 Ranking of emission rates for the four wall covering materials

(a) TVOCs

Rank	µ-CTE 15-30 min	FLEC 3 days	FLEC 28 days
1	1	1	1
2	2	2	2
3	3	4	3 [1]
4	4	3 [1]	--

(b) TXIB

Rank	µ-CTE 15-30 min	FLEC 3 days	FLEC 28 days
1	1	1	1
2	2	2	2
3	3	3	3
4	4	4	---

(c) Texanol

Rank	µ-CTE 15-30 min	FLEC 3 days	FLEC 28 days
1	3	1	1,2,3 [1]
2	1	2	---
3	2	3	---
4	4 [1]	4 [1]	---

(d) 2-EHA

Rank	µ-CTE 15-30 min	FLEC 3 days	FLEC 28 days
1	1	2	2
2	2	1	1
3	4	4	3 [1]
4	3 [1]	3 [1]	--

[1] compound not detected in these samples

Sampling after a short period of exposure of these materials using both techniques showed the presence of some more volatile compounds which were not observed after 3 and 28 days using the FLEC. In the extended test of wall covering 3 in the µ-CTE at 40 °C these compounds were no longer detectable in the sample taken two hours after the start of the test. The use of the slightly enhanced temperature in the µ-CTE test is

therefore resulting in an accelerated reduction in the emissions. For wall covering 1 the range of aliphatic hydrocarbons was still just detectable two hours after the start of the μ-CTE test. It is expected that a sample taken from this material after a slightly longer equilibration period, perhaps 2.5 hours, will show only the compounds detectable in the 3 and 28 day FLEC test. Another possibility, if it is required to reduce the test time, would be to investigate the use of a temperature above 40 °C for this material.

3.3.3.7 Vinyl floor tile

A chromatogram showing emissions from a portion of the second batch of vinyl floor tiles tested in the μ-CTE at 40 °C is given in Figure 3-33. The dominant compounds emitted from this material were identified as methyl isobutyl ketone (MIBK), butyl acetate, ethylbenzene, xylenes and 2-ethylhexan-1-ol. It is interesting to note that, whereas 2-ethylhexan-1-ol had been observed as one of the dominant compounds emitted from the previous batch of this material tested in the μ-CTE and in a Nalophan bag (Section 3.3.2), the other two dominant compounds observed previously (toluene and cyclohexanone) were seen in much smaller amounts from the present sample. The portion of batch 2 of the floor tile tested in the FLEC (Figure 3-34), gave the same dominant compounds as observed in the μ-CTE test of batch 2 of this material, with the addition of dimethylformamide (DMF).

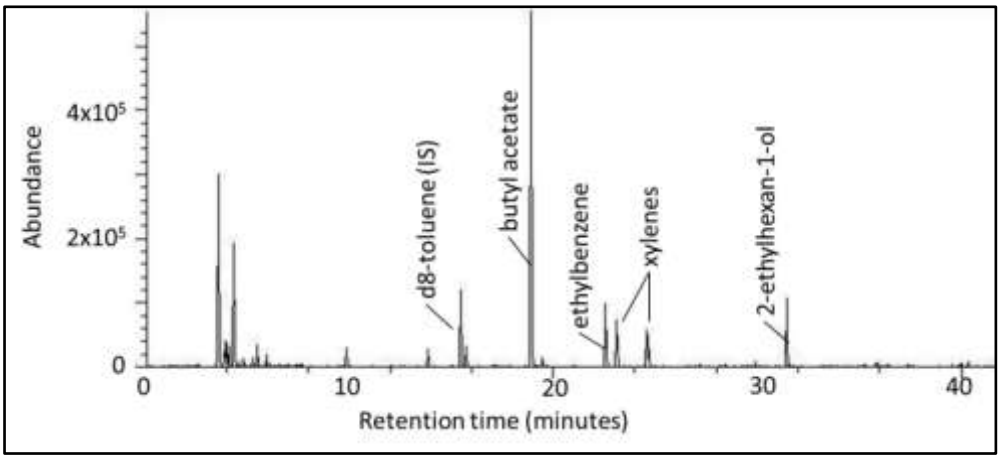

Figure 3-33 Chromatogram from sample of vinyl floor tile tested in the μ-CTE at 40 ºC

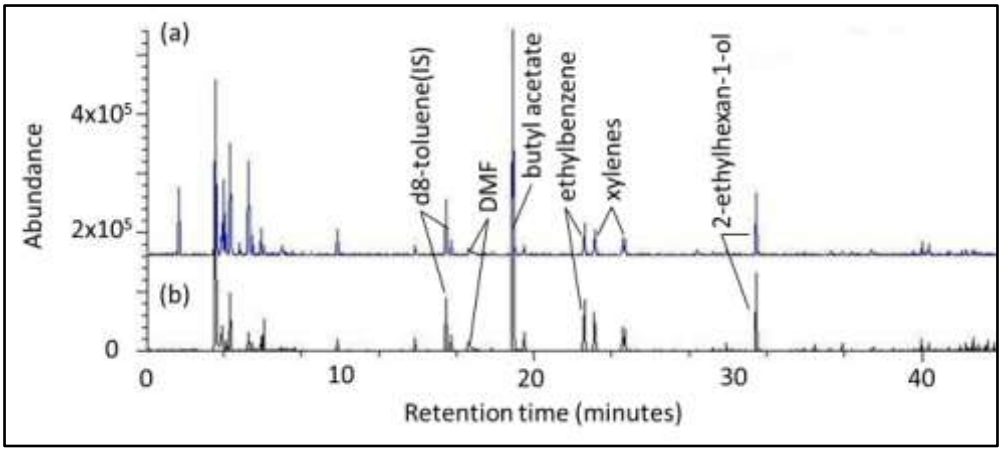

Figure 3-34 Chromatogram from sample of vinyl floor tile tested in FLEC (a) after one hour exposure (b) after 3 days exposure

Emission rates for the dominant individual compounds and TVOCs from the µ-CTE test of the vinyl floor tile are shown in Table 3-9. These are mean values of six replicate portions of the material tested in the µ-CTE. Relative standard deviations of < 20 % in each case were obtained, showing good homogeneity in this material. Emission rates of all the dominant compounds declined by about 50 % from the first to the last sampling period.

Table 3-9 Dominant compounds emitted from vinyl floor tile tested in the µ-CTE at 40 ºC

Compound	Mean emission rate (% RSD) (µg m^{-2} h^{-1}) (n=6)				
	1st tube	2nd tube	3rd tube	4th tube	5th tube
MIBK	47.7 (13.4 %)	38.7 (12.3 %)	33.1 (10.1 %)	27.5 (9.7 %)	24.9 (11.2 %)
Butyl acetate	1,070 (14.7 %)	898 (14.9 %)	785 (11.5 %)	683 (15.4 %)	598 (16.3 %)
Ethyl-benzene	111 (16.1 %)	95.3 (13.0 %)	82.3 (10.1 %)	70.9 (13.1 %)	63.1 (13.0 %)
Xylenes (sum of isomers)	129 (18.8 %)	109 (12.3 %)	86.1 (11.2 %)	69.2 (14.3 %)	55.9 (17.4 %)
2-Ethyl-hexan-1-ol	122 (19.8 %)	103 (15.5 %)	89.5 (11.7 %)	71.8 (16.9 %)	62.1 (19.2 %)
TVOCs	1,080 (18.5 %)	884 (16.6 %)	725 (12.4 %)	614 (13.8 %)	522 (18.1 %)

The emission profile for two of these compounds, butyl acetate and ethylbenzene, from a portion of this material tested using the FLEC are shown in Figure 3-35. Both compounds show a sharp decline over the first day followed by a more gradual decline. All the compounds dominant in early air samples from the FLEC test are still detectable at a low level after 28 days exposure, including DMF, at a level of around 5 μg m^{-2} h^{-1}.

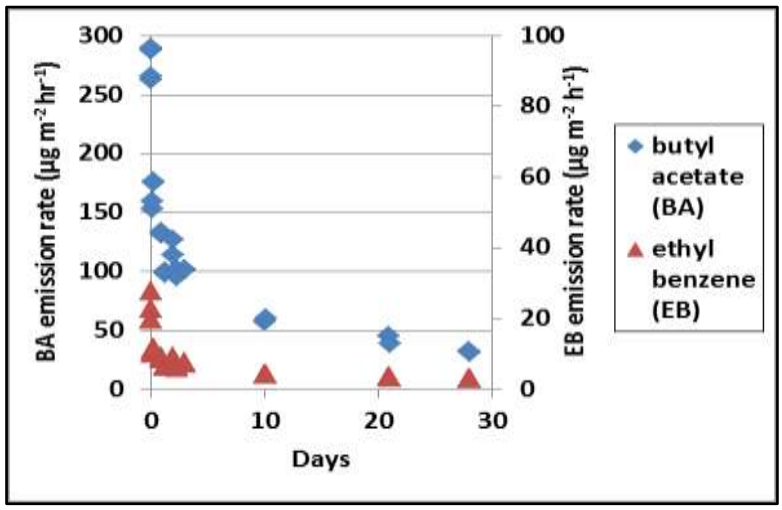

Figure 3-35 Emission profile for butyl acetate and ethylbenzene from vinyl floor tested using the FLEC

For this material, therefore, for all compounds other than DMF, any of the results from the μ-CTE test could be used to predict qualitatively those compounds which would be emitted after 3 or 28 days of exposure using the FLEC. This is demonstrated in Table 3-10 which shows the ranking of emission rates for measurable compounds in the first and last air samples from the μ-CTE test and those from the 3 and 28 days in the FLEC test. Butyl acetate was the compound observed in the largest amounts in each sample and (if DMF is not considered) MIBK is the compound found in the smallest amounts in each case. The ranking of the other compounds (ethylbenzene, xylenes and 2-ethylhexan-1-ol) differs somewhat between the samples, whereas in actual fact the emission rates were very similar for these compounds in each case. While DMF was only observed at a low level after 28 days exposure in the FLEC, it occurs on four of the target list identified as part of this project [and has a very low 'lowest concentration of interest' or LCI value according to the AgBB scheme (AgBB, 2012)] so is an important compound to determine. Further tests with a different portion of this material examined

using the FLEC and exploration of different temperatures with the μ-CTE are required to investigate why this compound was observed in the FLEC test but not from the μ-CTE.

Table 3-10 Ranking of emission rates for the vinyl floor tested in the μ-CTE and FLEC

Compound	μ-CTE		FLEC	
	15-30 min	105-120 min	3 days	28 days
MIBK	5	5	6	6
DMF	--- [1]	---	2	3
Butyl acetate	1	1	1	1
Ethylbenzene	4	2	5	5
Xylenes (sum of isomers)	2	4	3	2
2-ethylhexan-1-ol	3	3	4	4

[1] compound not detected in these samples

3.4 Conclusions

The main aim of this chapter was to examine the benefits and limitations of using screening methods for testing emissions of VOCs from materials. One important benefit of the use of screening methods over reference methods for emissions testing is cost. The smaller and simpler equipment involved compared with a large scale chamber results in quicker and cheaper tests. These could be used by a manufacturer as a first test prior to committing to the expense of testing using the reference method by an independent laboratory. A quicker test is also important, in the case of quality control, to warn a manufacturer as soon as possible of any change or problem in the manufacture that might prevent a batch of material achieving the required emission limits. The μ-CTE method has been found to have a number of advantages over the bag sampling method for the screening of samples of materials for emissions, including the possibility of sampling just from the exposed surface of a material and having lower background levels. The dynamic nature of the μ-CTE process also mirrors more closely that of a larger scale emissions test than is the case for the bag method.

Screening tests would also be useful for a manufacturer to investigate if any modifications to their products have an effect on the emissions and as a routine quality

control test. For this it is important to identify any such effects as soon as possible, and results obtained in the present project suggest that, using a slightly elevated temperature to accelerate the test, results can be obtained within a day. If it is required to be able to predict the emissions occurring from the longer exposure times specified in the reference methods, however, it appears that, from the findings for the materials examined using the μ-CTE during this study, the test temperature and equilibration time, need to be determined separately for each material.

The small size of the sample examined during a screening test can be advantageous for increased understanding of the source of emissions through comparison of emissions from different areas of a material or components of a product. However, this can also prove to be a limitation of screening tests in the case of inhomogeneous materials, where very different results can be obtained depending on the portion of the material tested. A greater number of replicate samples are therefore required to characterise the emissions in the case of such materials. However, inhomogeneity in materials was found, from the materials tested in this project, to also be a potential issue for sampling using the FLEC as well as for smaller scale tests. Further studies on the repeatability obtained from material emissions tests are required.

Aspects of this work were presented at three conferences as follows: μ-CTE and Nalophan bag tests at two temperatures (Indoor Air 2011 conference, Austin, Texas), μ-CTE tests of door and window samples (Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 2012, Cranfield) and μ-CTE tests of a range of materials (Healthy Building 2012 conference, Brisbane, Australia). Details of the papers, which were published in the proceedings of these conferences, can be found in Appendix G.

4 INVESTIGATION INTO THE EFFECT OF USE OF A MULTI-SORBENT TUBE ON COMPOUNDS DETECTED IN MATERIAL EMISSIONS USING TENAX TA SORBENT

4.1 Introduction

As discussed in the literature review (Section 1.5.1), informative Annex D of ISO 16000-6:2011 describes the use of multi-sorbent tubes to extend the volatility range of compounds which can be determined in one sample. The normative section of the standard requires the use of a Tenax TA tube and this sorbent has been applied routinely for emissions testing over a number of years. If the potential advantages of using multi-sorbent tubes are to be exploited, it is important to check that none of the compounds detected on a Tenax TA only tube are compromised. The second objective of the project was to compare the performance of Tenax TA and multi-sorbent tubes for compounds which would be defined as VOCs. This objective was investigated in two different ways. The first of these involved parallel sampling of a range of material emissions using Tenax TA and multi-sorbent tubes. The second involved a study of the recovery of a mixture of VOCs from tubes containing both sorbent types which were loaded from a standard atmosphere of these compounds. This study included an investigation of the stability of compounds on the sampler during storage prior to analysis, which is an important aspect of the performance of chemicals on sorbents.

A number of factors could affect the stability of compounds on sorbent tubes. Tubes used for material emissions testing are exposed to a humid environment, for example ISO 16000-9:2006 requires testing at 50 % RH, and the presence of moisture on sorbent tubes can affect the storage stability of some compounds (Prado et al., 2006). Also the volume of air sampled during material emissions testing is typically 1 to 5 litres. For multi-sorbent samplers, different sampling volumes will result in the analytes being distributed differently across the tube packing which might have an effect on their stability. The loading level of the analytes on a sorbent tube has also been found previously to have an effect on stability on storage (Crump et al., 2008; Volden et al., 2005). It is recommended that multi-sorbent samplers are stored in a refrigerator prior to

analysis (BS ISO 16000-6, 2011), but data on the benefit of this is lacking. Another factor to be considered is storage time. ISO 16000-6:2011 recommends that multi-sorbent tubes be analysed as soon as possible and within four weeks of sampling. Confirmation of stability on the sampler over periods of up to four weeks is therefore important for the emissions test samples. The study therefore sought to investigate the effects of humidity, sample volume, loading level, storage temperature and storage time on the performance of selected VOCs of interest with regard to material emissions.

4.2 Methods

4.2.1 Emissions tests using two sorbent types

The four wall covering materials tested using the μ-CTE and the FLEC as part of the study of screening techniques (Chapter 3) included sampling onto both Tenax TA and multi-sorbent tubes. Using the μ-CTE, three replicates samples were taken in each case onto tubes packed with Tenax TA and three onto tubes packed with MS2 (Quartz/Tenax TA/Carbopack X). Using the FLEC, duplicate sampling was undertaken using the two sorbent types for two of the wall covering materials, with sequential sampling onto the two sorbent types being undertaken for the other two materials.

4.2.2 Stability of check standard VOCs on multi-sorbent tubes

Nine of the 'check standard' compounds selected as representative of the range of compounds of interest in material emissions testing (see Section 1.4.1) were used to compare the stability performance of Tenax TA and multi-sorbents. These compounds were n-hexane, methyl isobutyl ketone (MIBK), toluene, butyl acetate, cyclohexanone, 1,2,3-trimethylbenzene (123-TMB), phenol, 4-phenyl-cyclohexene (4-PCH) and n-hexadecane. This part of the project was undertaken in collaboration with the Health and Safety Laboratory (HSL) and so was able to build on their experience in the development of a material emissions proficiency testing (PT) scheme using these compounds (see Section 1.4.3). The other two check standard compounds, hexanal and BHT, were not included as earlier studies at HSL had found them not to be stable during storage on Tenax TA. For the present study tubes packed with Tenax TA and those packed with both multi-sorbent combinations described in Section 2.3.1 were compared.

The study investigated compounds loaded at three levels to cover typical loadings used in material emissions testing. The effects of humidity and air volume were combined, so samplers exposed to VOCs in a humid atmosphere were also flushed with humid air. Loading of samplers was undertaken over one day by HSL staff at their laboratory in Buxton. The loading rig employed had been developed by HSL in accordance with an international standard method for the continuous production of stable gas mixtures using a motorised syringe (ISO 6145-4, 2004). The syringe continuously injects the VOC mixture in a methanol diluent into a stream of air (Plate 4-1). After mixing, the VOC containing atmosphere is directed into an exposure chamber where loading of up to 30 sorbent tubes takes place (Butler et al., 2012).

Plate 4-1 HSL's tube loading rig (supplied by HSL, 2013)

An experimental plan was developed to maximise the number of combinations of sampling and storage conditions which could be tested using four runs (batches) on the loading rig. The bulk of the samples were loaded with nominally 100 ng (equivalent to sampling 5 litres of a 20 µg m^{-3} atmosphere) of each component using tubes packed with MS1 (quartz wool/Tenax TA/Carbograph 5TD). A smaller number of tubes packed with Tenax TA and MS2 (quartz wool/Tenax TA/Carbopack X) were tested and some tubes packed with MS1 were loaded with nominally 40 ng and some with nominally

500 ng of each component. Five replicates of each set of loading/storage conditions were prepared for the 100 ng loading level and four replicates for the higher and lower levels. The air flow was continued following loading of the tubes to give a total volume of 1 litre in the case of those loaded in a dry atmosphere (<3 % RH), this was in order to purge off the methanol diluent. In the case of the tubes loaded in a humid atmosphere, a humidity of 40 % was achieved and the air flow was continued to give a total volume of 5 litres.

Eight of the loaded Tenax TA tubes and eight of the loaded multi-sorbent tubes, taken from random positions in the loading rig and from each of the four batches, were analysed at HSL as quality control (QC) samples. In addition 11 conditioned but un-exposed tubes, including some of each sorbent type, accompanied the tubes and were stored and analysed with them to act as blanks. The sampled and blank tubes were returned to the IEH laboratory and were analysed on the TD-100/GC/MSD system in batches over a period of 4 weeks from the time of loading.

Details of the loading and storage conditions and the schedule for analysis of the samplers are given in Table 4-1 and details of the storage conditions and analysis schedule for the blank tubes are given in Table 4-2. Analysis of the tubes identified for immediate analysis was undertaken as promptly as possible (given the need for the tubes to be transported to the laboratory) and was completed within four days of loading. Each of the sets of replicate tubes were analysed in one analytical sequence to minimize analytical imprecision. The samplers stored at room temperature were exposed to nominally 20 ºC with a range of 20-22 °C and the remainder were placed in a refrigerator at 5 °C. The end-caps of the refrigerated tubes were re-tightened one hour after they had been placed in the refrigerator. Tubes were removed from the refrigerator one hour before analysis. The ‘1 week’ samples were analysed eight days after loading and the ‘2 week’ samples were analysed 14 days after loading. The remainder of the samples were analysed between 29 and 32 days of loading.

Table 4-1 Details of tubes loaded, storage conditions and analysis schedule for tubes used for investigation of stability of nine VOCs on different sorbents

Batch	Loading conditions	Tubes loaded	Nominal loading level (ng)	Storage temperature (ºC)	Analysis schedule		
					Number of tubes	Sorbent	Time
1 and 2	Wet [a]	10 x Tenax TA, 35 x MS1, 10 x MS2 for QC: 3 x Tenax TA, 1 x MS1, 1 x MS2	100	N/A	5	Tenax TA	immediate
				20	5	Tenax TA	4 weeks
				N/A	5	MS1	immediate
				20	5	MS1	1 week
				5	5	MS1	1 week
				20	5	MS1	2 weeks
				5	5	MS1	2 weeks
				20	5	MS1	4 weeks
				5	5	MS1	4 weeks
				N/A	5	MS2	immediate
				20	5	MS2	4 weeks
3	Dry [b]	10 x Tenax TA, 15 x MS1 for QC: 3 x Tenax TA, 2 x MS1	100	N/A	5	Tenax TA	immediate
				20	5	Tenax TA	4 weeks
				N/A	5	MS1	immediate
				20	5	MS1	4 weeks
				5	5	MS1	4 weeks
4a	Wet	12 x MS1 for QC: 1 x Tenax TA, 2 x MS1	40	N/A	4	MS1	immediate
				20	4	MS1	4 weeks
				5	4	MS1	4 weeks
4b	Wet	12 x MS1 for QC: 1 x Tenax TA, 2 x MS1	500	N/A	4	MS1	immediate
				20	4	MS1	4 weeks
				5	4	MS1	4 weeks

[a] 'Wet' denotes 40 %RH and extra air purge; [b] 'Dry' denotes <3 %RH

Table 4-2 Details of storage conditions and analysis schedule for blank tubes used as part of investigation of stability of nine VOCs on different sorbents

Batch	Loading conditions	Tubes loaded	Nominal loading level (ng)	Storage temperature (ºC)	Analysis schedule		
					Number of tubes	Sorbent	Time
Blanks	N/A	2 x Tenax TA, 7 x MS1, 2 MS2	N/A	N/A	1	Tenax TA	immediate
				N/A	1	MS1	immediate
				N/A	1	MS2	immediate
				20	1	MS1	1 week
				5	1	MS1	1 week
				20	1	MS1	2 weeks
				5	1	MS1	2 weeks
				20	1	Tenax TA	4 weeks
				20	1	MS1	4 weeks
				20	1	MS2	4 weeks
				5	1	MS1	4 weeks

4.3 Results and Discussion

4.3.1 Emission tests using two sorbent types

Emission rates obtained using Tenax TA and the multi-sorbent tube MS2 were compared for TVOCs and dominant individual compounds which occurred in the emissions from the four wall covering materials investigated. Mean emission rates found in these tests separate according to sorbent type are given in Appendix D. Results obtained for the first 15 minute sample from wall covering 1 tested in the μ-CTE at 23 ºC separated according to sorbent type are shown in Figure 4-1. The six individual compounds and TVOCs all show good agreement in the mean emission rate obtained for the each sorbent. The corresponding results for wall covering 2 tested in the μ-CTE at 23 °C (Figure 4-2) show a similar pattern.

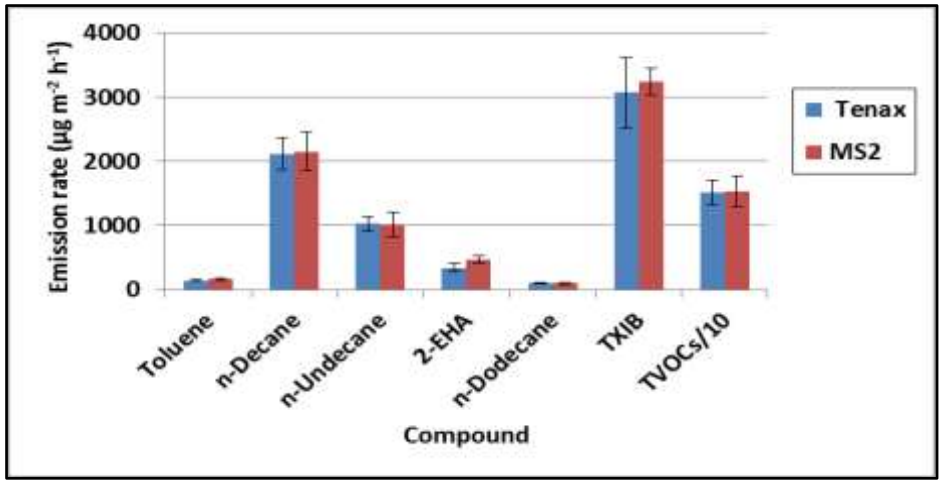

Figure 4-1 Mean emission rates of dominant compounds and TVOCs in first sample taken from wall covering 1 in µ-CTE at 23 ºC separated according to sorbent type (error bars are standard deviation)

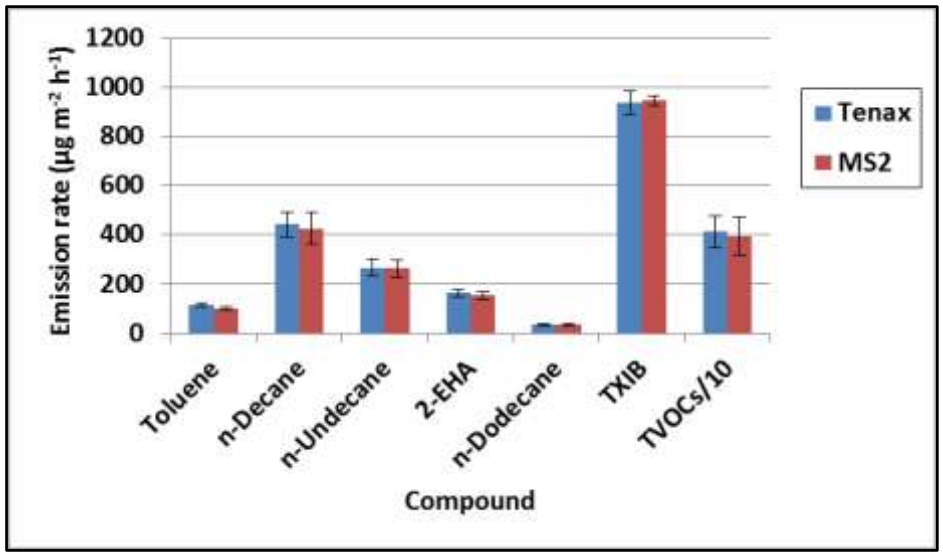

Figure 4-2 Mean emission rates of dominant compounds and TVOCs in first sample taken from wall covering 2 in µ-CTE at 23 ºC separated according to sorbent type (error bars are standard deviation)

For wall covering 3 (Figure 4-3), tested in the µ-CTE at 40 °C, differences were observed in the mean amounts of individual compounds and TVOCs determined using the two sorbents. The standard deviations for these results were however also high, suggesting that the differences are due to sample inhomogeneity rather than the sorbent. In these tests the emissions from three chambers containing different portions of a

material were tested using each sorbent type. With hindsight, a better study design for the purpose of testing performance of sorbents using an inhomogeneous material might have been to split the flow from one portion of material contained within a chamber.

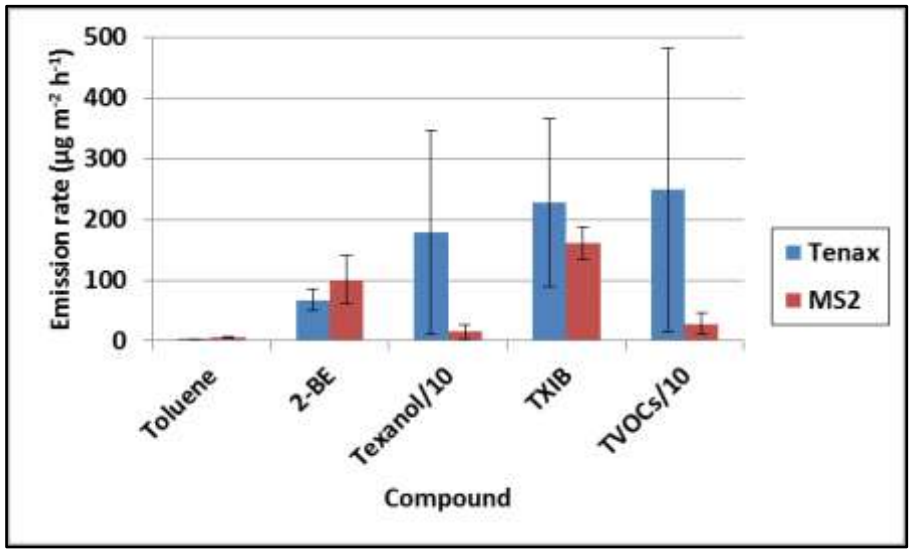

Figure 4-3 Mean emission rates of dominant compounds and TVOCs in first sample taken from wall covering 3 in µ-CTE at 40 °C separated according to sorbent type (error bars are standard deviation)

Emission rates for dominant compounds and TVOCs obtained using both sorbents for all four materials tested in the µ-CTE at 23 °C and 40 °C were compared using Student's t-tests. Results obtained are included in Appendix D. Although the high variability in some of the samples tested in the µ-CTE makes identification of any difference between emission rates for the two sorbents more challenging, 53 sets of replicate values with an RSD of ≤ 20 % for a particular compound were identified from the 82 data sets where quantifiable amounts were found from each chamber. A statistically significant difference between amounts of these compounds was obtained for just five of the 53 pairs of replicate samples. Two of these instances were due to a significantly greater mean amount of toluene for MS2 than for Tenax (whereas nine data sets showed no difference in the mean toluene value for the two sorbent types). Likewise one instance of a greater amount of TVOCs being found on MS2 than on Tenax was observed (whereas 11 data sets showed no such difference for TVOCs). Texanol and TXIB each registered one instance of a greater mean emission rate being

observed for Tenax than for MS2 (with two and 13 data sets respectively giving no such difference for these compounds). Therefore, for the vast majority of these data sets, no significant difference between the mean amounts of these compounds found on the two sorbent types was identified.

Using the FLEC, duplicate sampling onto the two sorbent types had been undertaken for the test of wall covering 1. Emission rates obtained for n-undecane and TXIB over the first three days of the test and separated according to the two sorbent types are shown in Figure 4-4. Emission rates of TVOCs and the dominant individual compounds were compared using paired t-tests (P = 0.05). No significant difference between the sorbents was found for n-decane, n-undecane, TXIB or TVOCs and, while a statistically significant difference was found for 2-ethylhexanoic acid, the actual difference between the mean values was only 5 %.

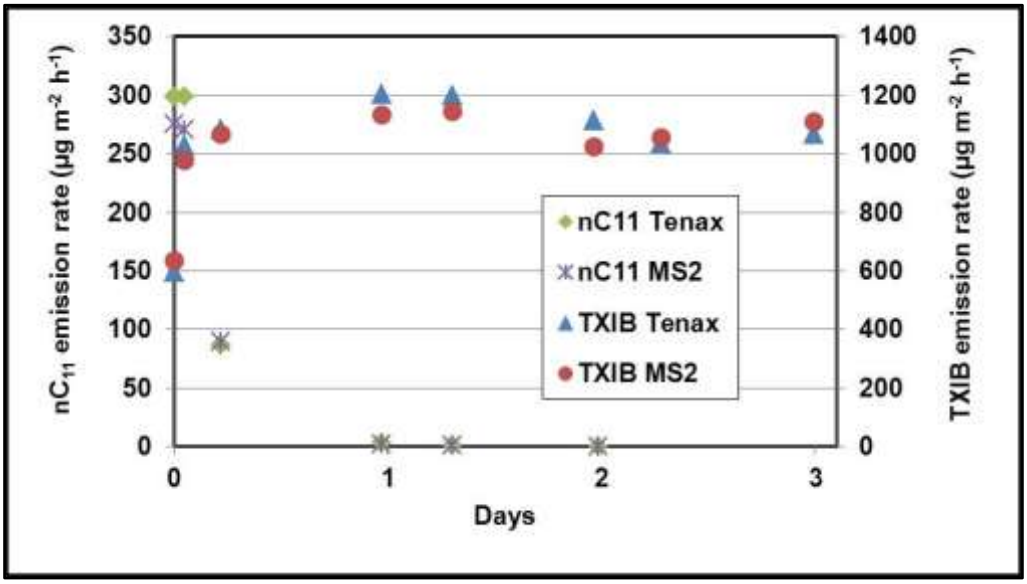

Figure 4-4 Emission rates of n-undecane and TXIB from wall covering 1 tested using the FLEC separated according to sorbent type

For the tests of portions of wall coverings 2 and 3 using the FLEC, sequential sampling onto the two sorbent types had been undertaken. The emission profiles for n-decane and TXIB from wall covering 2, separated according to sorbent type, are shown in Figure 4-5 and those for 2-butoxyethanol (2-BE) and Texanol from wall covering 3 are

shown in Figure 4-6. Comparable amounts of these compounds are again observed on the two sorbent types.

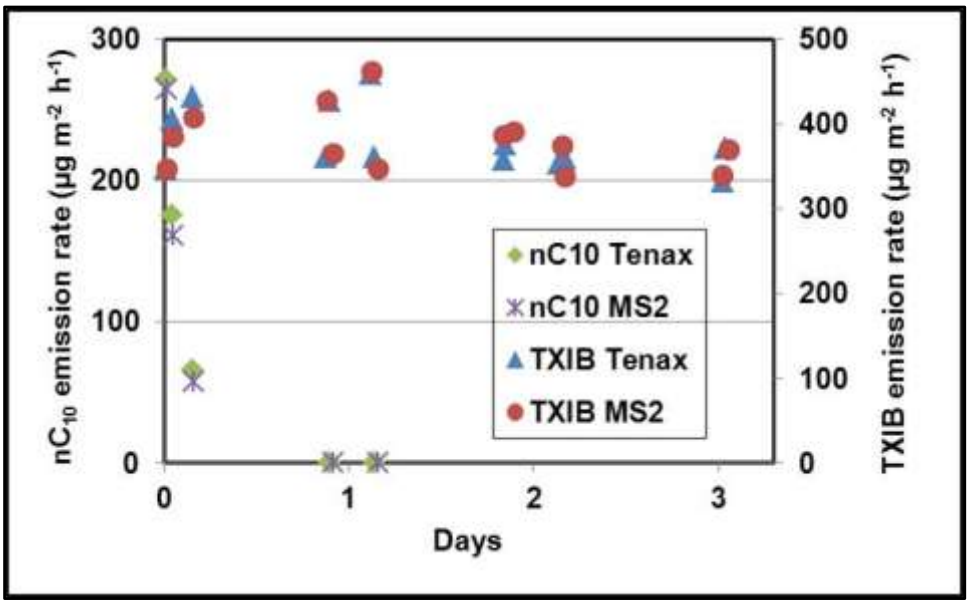

Figure 4-5 Emission rates of n-decane and TXIB from wall covering 2 tested using the FLEC separated according to sorbent type

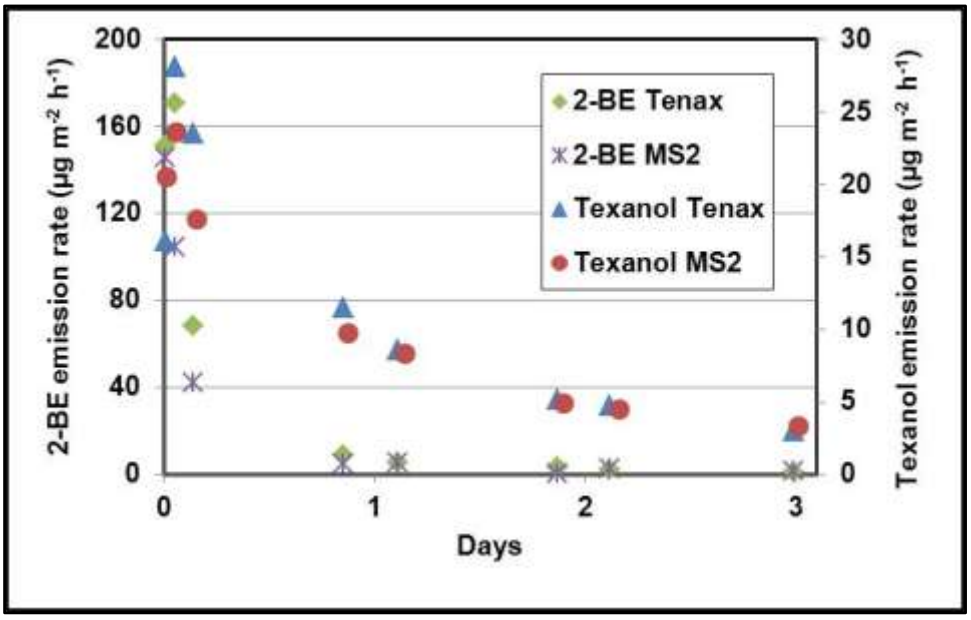

Figure 4-6 Emission rates of 2-butoxyethanol (2-BE) and Texanol from wall covering 3 tested using the FLEC separated according to sorbent type

The emission profile for toluene and TXIB released from wall covering 4 is shown in Figure 4-7. Duplicate sampling had been undertaken for this material. No significant difference between the sorbents was found for toluene, n-decane, 2-ethylhexanoic acid and TXIB. For TVOCs a statistically significant difference between the mean emission rates was observed, though the actual difference between the mean values was only 3 %. The findings of these FLEC tests build on those of the µ-CTE to show that the two sorbent types can give comparable results for TVOCs and nine individual compounds covering the volatility range of toluene to TXIB.

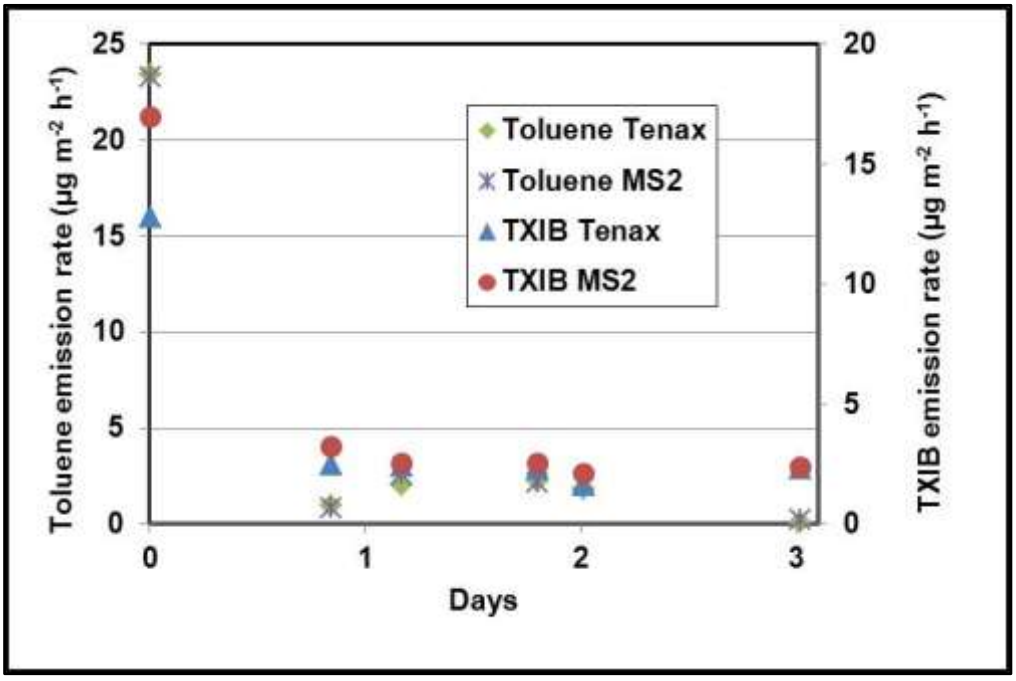

Figure 4-7 Emission rates of toluene and TXIB from wall covering 4 tested using the FLEC separated according to sorbent type

4.3.2 Stability of check standard VOCs on multi-sorbent tubes

4.3.2.1 Recovery of analytes from different sorbents and loading conditions with immediate analysis

As the experimental plan for this test shows (Table 4-1), seven sets of replicate tubes were analysed at IEH immediately after loading. The repeatability of these was found to be typically around 3 % or better, with values of 5 % being obtained for butyl acetate and n-hexadecane in two sets of tubes and values of between 5 and 10% being obtained

for phenol in five sets of tubes. The % recoveries, compared to amounts found on analysis of the QC tubes (reported by HSL), were generally between 92 and 119 %, with higher values (112-129 %) being found for butyl acetate (the reason for which was not identified) and a higher range of 89-129 % being obtained for phenol. These results show that comparable precision is being obtained for the two laboratories and differences in recoveries between the laboratories are acceptable. Amounts of the nine compounds found for each set of immediately analysed tubes are given in Table D-17 in Appendix D and recoveries compared to those found on the QC tubes are given in Table D-18.

Analysis of the blank tubes at IEH, either immediately or after storage in the laboratory or in a refrigerator, gave, in most cases, no detectable amounts of any the compounds of interest. Exceptions to this were toluene and phenol which were detected in all of the blank tubes. The amount of toluene found ranged from 4 to 11 ng on the tube, with a mean value of 6 ng; whereas that for phenol ranged from 9 to 35 ng with a mean of 19 ng. No pattern was observed in the amounts of these two compounds found, i.e. the amount did not appear to be related to the sorbent or storage conditions or to increase with time stored. This occurrence could explain increased variability in these two compounds, particularly for the low loading levels.

In order to compare the recoveries of target analytes from the different sorbents and loading conditions, the amounts of each compound found from analysis of tubes loaded onto Tenax TA in a dry atmosphere were taken as 100 %. Relative recoveries for the multi-sorbent tubes and for tubes loaded in a humid atmosphere (plus extra air purge) are given in Table 4-3. For n-hexadecane it was only possible to compare amounts on sets of tubes from the same loading batch as the results of GC tubes had found differences in the amounts of this compound loaded between batches. This compound is at the high boiling point end of the VOC volatility range and this was thought to have caused the variation. The values obtained ranged between 93 and 107 %, with three quarters of the values between 95 and 102 %. Data analysis employed Student's t-tests for comparisons of two groups and one way analysis of variance (ANOVA) (both at $P = 0.05$) for comparisons of more than two groups. Significant differences in recoveries for

the different sorbents and loading conditions for each analyte studied are shown in Table D-19.

Table 4-3 Recoveries for the sets of tubes of nominal loading 100 ng analysed immediately as part of the study of storage stability on Tenax TA and multi-sorbents

Sorbent	Loading conditions	Mean % recovery compared to that obtained from Tenax tubes loaded in a dry atmosphere (n = 4 - 5)								
		n-Hexane	MIBK	Toluene	Butyl acetate	Cyclohexanone	Phenol	123-TMB	4-PCH	n-Hexadecane
Tenax TA	Wet	95	96	95	96	96	93	101	102	NR [a]
MS1 [b]	Dry	102	96	97	96	94	100	97	96	100
MS1	Wet	100	95	94	93	93	99	100	100	NR
MS2 [c]	Wet	101	95	96	94	94	107	96	97	NR

[a] NR = no tubes available for comparison; [b] MS1 = quartz wool/Tenax TA/Carbograph 5TD; [c] MS2 = quartz wool/Tenax TA/Carbopack X

While statistically significant differences were found for some of the compounds and sorbents or loading conditions, no consistent pattern was observed which might suggest that the humid atmosphere and air purge always gives a lower recovery for this range of compounds and no consistent difference in recovery between the sorbents was detected. Also, given that the number of tubes involved meant that these analyses were undertaken over two analytical sequences, the magnitude of the differences in recovery is small (mean of <4 %). So gas phase loading of a mixture of VOCs onto Tenax TA in an atmosphere of 40 % relative humidity and with an air volume of 5 litres (as might be used in material emissions sampling), with analysis within 4 days, gave amounts which are comparable to those obtained from loading onto this sorbent in a dry atmosphere. Likewise recoveries of the target analytes from two different multi-sorbent tubes loaded in either a dry or wet atmosphere and analysed within 4 days are comparable to that from a Tenax TA tube.

4.3.2.2 Storage stability for single and multi-sorbent tubes over 4 weeks

The storage stabilities of tubes after 1, 2 and 4 weeks were examined as % recoveries of the different compounds on the respective days of analysis compared to the levels obtained on initial analysis with the same sorbent and loading conditions. Figure 4-8 shows the mean % recoveries obtained for toluene. Tubes loaded with nominally 100 ng onto MS1 in a humid atmosphere and stored at room temperature for 1 and 2 weeks before analysis gave recoveries of 100 and 101 % respectively of the initial level, while tubes loaded with the same conditions and stored for these periods in a refrigerator gave recoveries of 102 and 101 % respectively. Tubes with the same loading conditions and

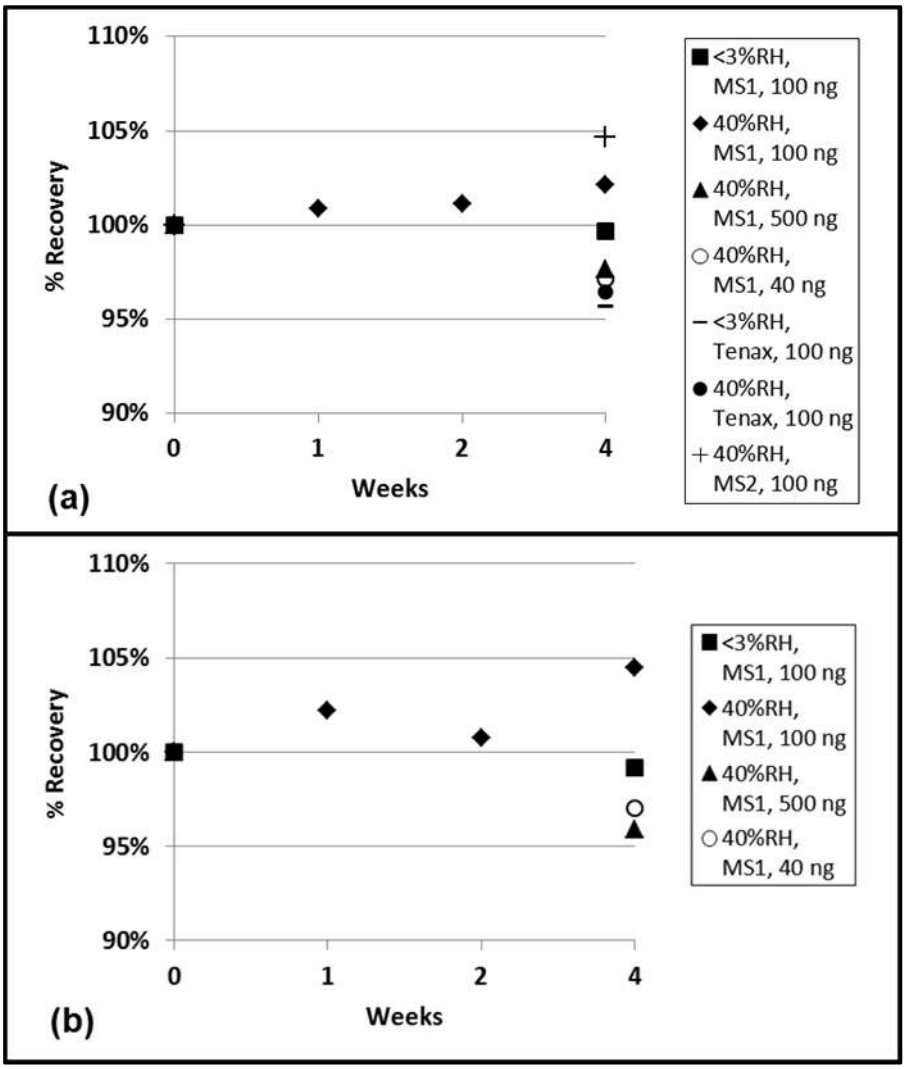

Figure 4-8 Percentage recoveries for toluene stored for up to 4 weeks after loading (a) at room temperature and (b) in a laboratory refrigerator

stored for 4 weeks before analysis gave a recovery of 102 % for those stored at room temperature and 104 % for those stored in a refrigerator. Recoveries for this compound from all sorbents and loading levels and conditions ranged from 96 to 105 % for tubes stored for 4 weeks at room temperature and 96 to 104 % for those stored in a refrigerator.

Results obtained for all compounds for each combination of loading and storage conditions are given in Table 4-4. The majority of the recoveries are close to 100 %, with all except seven individual values being within the range 90 to 106 %. The remaining values (having recoveries of ≥87 %) are all for the four least volatile compounds investigated (phenol, 123-TMB, 4-PCH and n-hexadecane) and a storage period of four weeks. Three of these values are for phenol, which is subject to high variability and one is for n-hexadecane for which the amount loaded (29 ng) was significantly lower than the target loading and is therefore also subject to higher variability. ANOVA and t-tests (P = 0.05) were used to identify statistically significant differences between recoveries for sets of tubes with a particular combination of sorbent and loading conditions and the different times stored. A number of significant results were obtained and these are shaded in Table 4-4. There was a tendency for more significant differences to be observed with the less volatile compounds investigated, in particular for n-hexadecane which had the lower amounts loaded. Also for one set of tubes (those loaded with 500 ng of each component in a humid atmosphere and stored for 4 weeks) significantly lower recoveries than for the initially analysed tubes were obtained for all compounds except n-hexane. However, as the great majority of recoveries were ≥ 90 % [which has been recommended by the US National Institute for Occupational Health and Safety as a sample storage criterion for air samplers (Kennedy et al., 1996)], the findings of this study therefore meet this criterion. These findings are also in agreement with the recommendation for tubes sampled as part of emissions tests to be analysed as promptly as possible and within 4 weeks.

Table 4-4 Recoveries for the different sorbents, analyte mass, loading conditions, storage times and temperatures

Sorbent	Nominal mass (ng)	Loading conditions	Storage time (weeks)	Storage temp. (ºC)	Mean % recovery compared to initial analysis for same sorbent (n = 4 – 5)								
					n-Hexane	MIBK	Toluene	Butyl acetate	Cyclo-hexanone	Phenol	123-TMB	4-PCH	n-Hexa-decane
Tenax TA	100	Dry	4	20	95 [a]	98	96	95	95	99	93	92	95 [b]
Tenax TA	100	Wet	4	20	95	96	96	93	92	88	91	89	90 [b]
MS1	100	Dry	4	20	98	101	100	94	95	92	89	89	85 [b]
MS1	100	Dry	4	5	96	100	99	97	98	103	96	97	90 [b]
MS1	100	Wet	1	20	96	100	101	100	100	93	99	98	NR [c]
MS1	100	Wet	1	5	98	102	102	102	101	105	101	99	NR
MS1	100	Wet	2	20	100	100	101	103	101	101	99	98	NR
MS1	100	Wet	2	5	98	100	101	104	101	99	99	99	98 [b]
MS1	100	Wet	4	20	99	104	102	97	96	93	93	94	95 [b]
MS1	100	Wet	4	5	100	102	105	99	98	98	97	95	94 [b]
MS2	100	Wet	4	20	100	105	105	96	96	91	96	94	92 [b]
MS1	40	Wet	4	20	101	101	97	104	100	93	98	96	99
MS1	40	Wet	4	5	101	101	97	106	102	100	99	99	99
MS1	500	Wet	4	20	100	98	98	97	98	88	99	98	94
MS1	500	Wet	4	5	97	97	96	96	97	87	98	96	92

[a] Highlighted cells show results which are significantly different (at the $P = 0.05$ probability level) from values obtained on initial analysis
[b] Actual loading for this compound significantly lower than the 100 ng nominal loading; [c] NR = no tubes available for comparison

Further statistical tests were undertaken to investigate specifically for differences in recovery on storage of these VOCs on the different sorbents and subject to the different loading conditions (details given in Table D-20). Again no consistent effect was found for the tubes loaded in a humid atmosphere and with the extra air purge. For the different sorbents, the only consistent difference found was for significantly greater amounts of n-hexane to be recovered for the multi-sorbent tubes than from Tenax TA in both tubes loaded in dry and humid atmospheres. As n-hexane is at the extremity of the volatility range for which Tenax TA is applicable (ISO 16017-1:2001), it is not unexpected that on storage the presence of the stronger sorbent in the multi-sorbet tube would result in an improved recovery of this compound than from Tenax TA alone. For the less volatile compounds there was a potential concern regarding the possibility of their migration to the stronger sorbent on storage with resulting poor recovery, but no evidence for this was found.

To investigate for any effect of the analyte loading level on the recovery, the mean % recoveries for the different loading levels of each compound after storage for 4 weeks either at room temperature or in a refrigerator were compared (Figure 4-9). Some low recoveries were obtained for phenol from the 500 ng loading level, but otherwise no consistent pattern was observed in these results, suggesting that, over the loading range tested, analyte loading does not have a significant effect on the recovery.

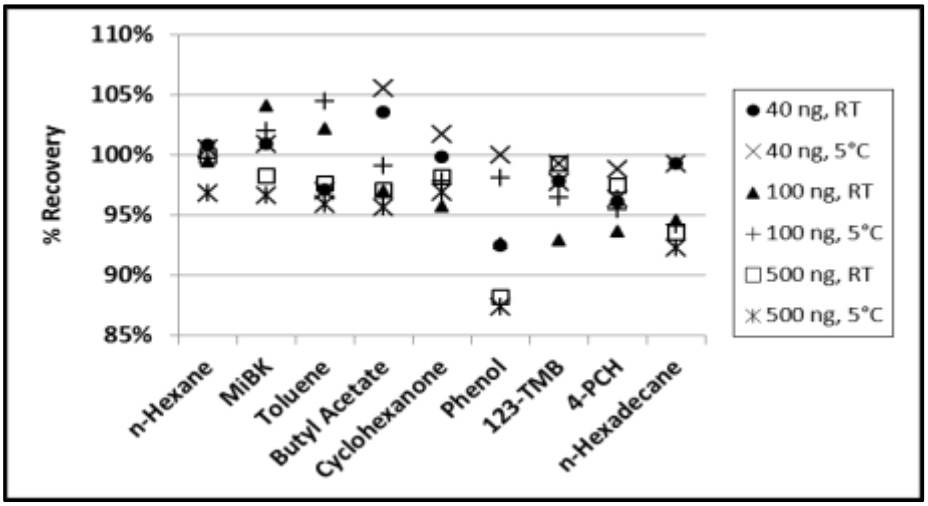

Figure 4-9 Percentage recoveries for the different loading levels of each compound after storage for 4 weeks at either room temperature or in a refrigerator

The final parameter tested in this part of the study was the effect of storage at room temperature (20-22 °C) or in a laboratory refrigerator (at 5 °C). T-tests (P = 0.05) were undertaken for each of the replicate tube sets which were stored for the same length of time at one of these two conditions. Sets available were 100 ng humid loading on MS1 with storage for 1, 2 and 4 weeks; 100 ng dry loading on MS1 with storage for 4 weeks; 40 ng humid loading on MS1with storage for 4 weeks and 500 ng humid loading on MS1 with storage for 4 weeks. Only one statistically significant difference for one analyte was observed from all six of the replicate sets of tubes (the 500 ng loading of n-hexane showed a significantly greater recovery for tubes stored at room temperature than was obtained for those stored in a refrigerator). The magnitude of this difference was only 3 %, so it can be concluded that, for these compounds, loading levels and sorbents, there is no advantage in refrigerating the tubes while they are awaiting analysis.

4.3.2.3 Comparison with previous studies

A further storage trial, of the same compounds loaded onto Tenax TA tubes in a dry atmosphere, was undertaken at HSL. The same loading rig was used as in the present study with a loading level of 100 ng. Results are reported in a joint paper covering both studies which has been prepared for submission to a relevant journal and is included in Appendix G. Tubes analysed periodically over a time period of 12 months gave recoveries typically within 5 % of the initial values. Greater variation (up to 20 %) was found for phenol, thought to be a result of artefact formation. The two studies, involving analysis at different laboratories, both show acceptable storage performance up to a period of 4 weeks for this set of compounds on Tenax TA tubes in the absence of moisture.

An earlier comparison conducted as part of the "certification of a reference material for aromatic hydrocarbons in Tenax" TA sorbent tube samplers (Vandendriessche et al., 1991) found a loading of 1,000 ng of toluene, in the presence of the same amount of benzene and xylene, to be stable during storage at either ambient temperature or in a refrigerator for 25 months. The storage recovery of 40 compounds at a loading of 10,000 ng on Tenax TA, including hexane, toluene, MIBK, butyl acetate and cyclohexanone, has also been reported (ISO 16017-1:2001). Recovery of MIBK, butyl

acetate and cyclohexanone were found to be equal to that of toluene after 5 and 11 months. Recovery recorded for hexane was 94 % after 5 months and 101 % after 11 months. In each case the precision, at 18 % and 26 % respectively, was significantly higher than observed for the other compounds studied. The findings of the present study are consistent with these results, suggesting that the lower loading levels are not resulting in a drop off in stability for these compounds. The repeatability issue observed with hexane on Tenax TA previously is not unexpected given the volatility of this compound, whilst the results of the present study suggest that its performance might be improved by the inclusion of a stronger sorbent.

One study which reported stability on some multi-sorbent tubes (Wright et al., 1998), involved testing 39 compounds including toluene, at a loading of ~300 ng, on various sorbents including three types of multi-bed sorbents for up to 21 weeks. ≥ 95 % recovery was found from Tenax GR/Carbopack B (the most similar sorbent combination to those used in the present study) which is again consistent with the findings from the present study.

Volden et al., (2005) investigated the performance of toluene and butyl acetate, amongst a mixture of eight other VOCs, loaded onto Tenax TA from the liquid phase and stored at 5 °C and ambient temperature for 7, 14 and 28 days. The findings for a 500 ng loading with storage at 20 °C (mean recovery of ≥ 90 %) are consistent with the present study, whereas recoveries obtained from a 50 ng loading level and following storage in a refrigerator were lower than found in the present study. The suggestion was that much of the drop off occurred between the day of exposure and 7 days. Immediate analysis was not possible in the present study, but the comparison between HSL's results from analysis of the QC tubes and IEH's initial analysis does not suggest that any decline in amounts on the tubes had occurred before the initial analysis was possible.

4.4 Conclusions

A comparison of Tenax TA and multi-sorbent tubes during emission testing of some materials has provided evidence of equivalent performance of the two types of tube for determination of TVOCs and nine individual compounds of varying volatility. Interpretation of the data was confounded to some extent by inhomogeneity in the

materials tested. Further experiments to compare sorbent performance could be undertaken using parallel sampling with the two tube types and or use of a more consistent material, such as a reference material. Development of reference materials for emissions testing was described in Section 1.4.4.

The storage performance of the two types of multi-sorbent tubes tested has also been found to be equal to that for Tenax TA for the VOC mixture formulated for quality assurance of analysis of material emissions. This is evidence therefore that multi-sorbent samplers tested can be applied to sampling of material emissions, with the expected benefit of improved performance for very volatile compounds (VVOCs), without compromising the VOC range. Work to evaluate this advantage for determining a range of VVOCs is described in Chapter 5. A recovery of within about 10 % of the amount loaded can be expected for four weeks storage for nine VOCs tested. The recommendation for tubes sampled as part of emissions tests to be analysed as promptly as possible, and within 4 weeks, therefore remains good advice for both Tenax TA and multi-sorbent tubes.

Storage at room temperature was found to give the same recoveries as obtained for tubes stored in a refrigerator. This precaution is therefore not necessary for this set of compounds. This would remove one possible source of contamination on the tubes from other volatiles which can be present in refrigerators and can enter tubes if caps loosen as a result of the temperature change. Tubes loaded in an atmosphere of 40 % relative humidity and with an extra air purge showed as good performance as those loaded in a dry atmosphere. While it would be of benefit to repeat this study with higher humidity levels, to reflect the slightly higher conditions used in emission tests, this study suggests that any effect of humidity is small.

The tests of wall covering materials in the µ-CTE using different sorbent types were presented at the Healthy Building 2012 conference, Brisbane, Australia. Details of the paper, which was published in the proceedings of the conference, can be found in Appendix G. The trial of storage of VOCs on different sorbent types has been drafted for submission to the Journal of Chromatography A (again see Appendix G for details).

5 INVESTIGATION INTO THE POSSIBILITY OF EXTENDING THE VOLATILITY RANGE OF COMPOUNDS WHICH CAN BE DETERMINED IN MATERIAL EMISSIONS USING TD/GC

5.1 Introduction

As identified in Section 1.5.1, there is a growing demand for the determination of compounds encompassing an increased volatility range in material emissions testing. There are two aspects to this, one is the existence of a suitable emission test method, which minimises sink effects which can be an issue with high boiling compounds, and the other is determining the emissions effectively with as few types of air sampler as possible to reduce costs. This is likely to involve a combination of sorbents contained within one sampling tube. One VVOC of particular concern, formaldehyde, currently requires the use of a different analytical technique, normally HPLC, for its effective determination (see Section 1.2.4.2). If a reliable method involving use of TD/GC for this compound were to be developed (as work described in Section 1.5.2 promises) this would provide a further cost saving. The method investigated by Veasey (2000) involves modification of the sampling tube to allow derivatisation and therefore the aim would not in this case be to determine other compounds using the same sampler at the same time.

Two sets of experiments using multi-sorbent tubes were conducted in support of objective 3 of the project. In the first of these, emissions tests using the same screening techniques applied in Chapter 4 were undertaken with sampling onto both Tenax TA and multi-sorbent tubes, the difference being that materials which were known to release either VVOCs or SVOCs were tested. Secondly both tube types were used to sample from atmospheres containing a generated mixture of VVOCs or an SVOC. These tests sought to develop procedures for assessing recovery/breakthrough of the selected compounds.

The final task in support of this objective was to investigate the possibility of determining formaldehyde using TD/GC. The method employed was that based on the

reaction of formaldehyde with 2-hydroxymethylpiperidine (2-HMP) [CAS number 3433-37-2] which was previously investigated by Veasey (2000). The reaction product resulting, formaldehyde oxazolidine [CAS number 6833-37-0], is volatile and amenable to analysis by GC. This reaction also forms the basis of a NIOSH (National Institute for Occupational Safety and Health) method for the determination of formaldehyde by GC with solvent desorption using toluene (NIOSH, 1994). The compounds involved are shown in Figure 5-1.

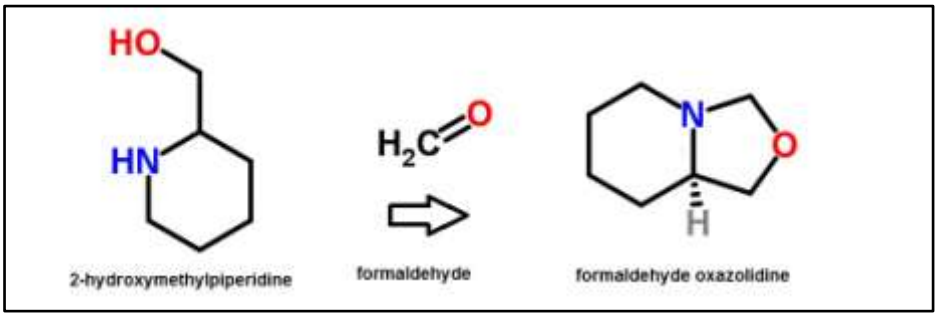

Figure 5-1 The reaction between 2-hydroxymethylpiperidine and formaldehyde

In order to investigate the performance of a method for the determination of formaldehyde it is necessary to have a stable source of formaldehyde and a reference method to use for comparison of its emission rate. For this a material known to be a source of formaldehyde was selected and its emissions were determined using the European standard method for determination of formaldehyde release from wood-based panels, EN 717-1:2004 (see Section 1.3.1.1). This method is based on the Hantzsch reaction between formaldehyde and acetylacetone [pentane-2,4-dione] in the presence of ammonium ions to give a compound (diacetyldihydrolutidine) which can be determined photometrically. The molecule also exhibits fluorescence (at 510 nm), so an alternative is to use fluorimetric determination giving an increase in both selectivity and sensitivity. The method has been found to give equivalent results to that specified in ISO 16000-3:2011, i.e. the determination of formaldehyde by active sampling using 2,4-dinitrophenylhydrazine (DNPH), solvent desorption and HPLC (Salthammer and Mentese, 2008). The acetylacetone method would also prove more economical than a method involving purchase of DNPH coated cartridges and analysis using HPLC, which is of particular benefit during development work. The reaction of formaldehyde with

acetylacetone and other β-diketones has also been applied in sensors which have been developed for the determination of this compound (Maruo and Nakamura, 2011; Maruo et al., 2010; Bunkoed et al., 2010).

5.2 Methods

5.2.1 Emission tests using two sorbent types

5.2.1.1 Composite door foam – source of VVOCs

The first material tested was the polyurethane (PU) foam insert from the composite door, which had previously been tested (see Chapter 3). Portions of the foam were freshly cut from the surrounding GRP (glass reinforced plastic), then placed in a chamber of the μ-CTE which had been pre-equilibrated at 23 °C with an air flow rate of 130 ml min^{-1}. An empty tube was connected to the outlet of the chamber and conditioned tubes attached using a cross piece connector. Duplicate sampling was undertaken using one tube containing Tenax TA and one containing MS1 (quartz wool/Tenax TA/Carbograph 5TD). The emissions were sampled for 15 minutes at a rate of 50 ml min^{-1} through each tube using TSI SidePak SP130 air sampling pumps. The experimental set up is shown in Plate 5-1.

Tests were undertaken on five different portions of foam, ranging in mass between 0.2 and 1.3 g, with varying numbers of pairs of tubes used to successively sample the emitted air to give a range of analyte loadings. One test was included for which the flow rate through the tubes was increased to approximately 80 ml min^{-1} and the sampling time to 60 minutes in order to check for breakthrough at a higher air volume. For this test, two tubes of each sorbent type were used in series connected with a brass union. Sampled tubes were stored at room temperature and analysed within one week on the TD-100/GC/MSD system using the analytical procedure described in Appendix A.5.

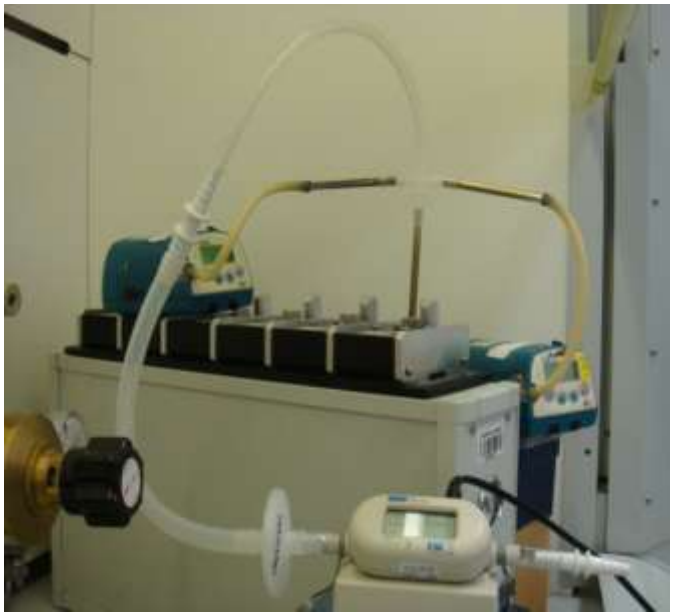

Plate 5-1 µ-CTE set up to undertake duplicate sampling

5.2.1.2 Foam sealant – source of VVOCs

A commercially available aerosol applied foam sealant was tested using both the FLEC and the µ-CTE. Immediately before each test the container was shaken vigorously as specified by the producer after which the material was sprayed into a moistened aluminium foil dish. The FLEC was placed over a glass desiccator and a flow rate of about 140 ml min^{-1} of 50 %RH air passed through. The freshly sprayed foam was placed in the desiccator and duplicate air sampling was undertaken using one Tenax TA tube and one MS1 tube, with a flow rate of 50 ml min^{-1} through each tube. The experimental set up is shown in Plate 5-2. Sampling was repeated periodically over the next 25 days with sample volumes ranging from 0.2 to 5 litres. For 12 of the sampling events two of each tube type connected in series were used. The temperature of the laboratory during the period of test ranged between 20 and 22 °C. With the µ-CTE, a temperature of 23 °C was used with periodic sampling over a 25 day period. A range of air volumes between 0.2 and 10 litres were sampled in order to provide further information about the C_4 hydrocarbons which had shown very high concentrations using the FLEC. Sampled tubes were stored at room temperature and analysed within one week on the TD-100/GC/MSD system using the analytical procedure described in Appendix A.5.

Plate 5-2 Foam sealant sample being tested using the FLEC

5.2.1.3 Wall covering – source of SVOCs

A fresh portion of one of the wall covering materials (wall covering 1), which had been tested previously as described in Chapter 3, was studied using the FLEC. Information provided by the supplier of the wall covering materials (see Section 2.1.3) stated that three plasticisers, all of which would be categorised as SVOCs, were used in the production of these materials. Two of these chemicals, diisononyl phthalate (DINP) and di-2-ethylhexyl terephthalate (DEHT), were acquired and analysed on the TD-100/GC/MSD system in order to determine their retention times and spectra. Modified analytical conditions were developed to give a sensitive method specifically for the determination of these two compounds. This involved a faster GC oven ramp rate to give a shorter GC run (50 °C for 1 minute, 10 °C/minute to 300 °C and hold for 15 minutes, total run time 41 minutes) and use of selected ion monitoring (SIM) ionisation mode on the MSD (see Section C.3.3). The material was cut to fit just inside the O-ring of the FLEC and placed on a base of aluminium foil. Samples were taken from the FLEC air outlet with Tenax TA and MS1 tubes over a four week period using air volumes of between 10 and 350 litres. Sampled tubes were stored at room temperature and analysed within one week on the TD-100/GC/MSD system using either full scan (FS) or SIM ionisation mode.

5.2.2 Tests of VVOC/SVOC atmospheres

5.2.2.1 VVOC atmosphere - using Nalophan bags

Nalophan sheeting of widths 21 cm and 36 cm and cut to lengths of between 50 and 120 cm were used in this part of the study. 10 VVOCs were selected for investigation, all of which appear on at least one target list of chemicals (Table 5-1). Two liquid mixes (A and B) each containing five of the compounds were prepared using a syringe to add the amounts of the compounds as shown in Table 5-1 to a glass vial. One end of a length of Nalophan sheeting was sealed by fan folding around a length of ¼ inch polyethylene tubing and secured using cable ties. The end of the tubing outside the bag was fitted with a ¼ inch nut and cap. A 0.05-0.1 µl aliquot of one of the VVOC mixes was spiked onto the inner surface of the Nalophan after which the second end of the bag was sealed by fan folding, turning over a 1 cm length and securing with a cable tie. The bag was filled with a measured amount of zero grade air, sealed and allowed to equilibrate at ambient temperature for 10 minutes.

Table 5-1 VVOCs studied in breakthrough experiments using Nalophan bags

Compound	CAS Number	Boiling point (°C)	Target lists found on [¶]	Amount added and mix
Acetaldehyde	75-07-0	21	b, d*, f, i, j, k, m, n	100 µl, A
Isoprene	78-79-5	34	k, †	100 µl, A
Dichloromethane (DCM)	75-09-2	40	b, i, j, k, n	100 µl, B
Methyl tertiary butyl ether (MTBE)	1634-04-4	55	i, j, n,	200 µl, B
Acetone	67-64-1	56	d*	200 µl, B
Chloroform	67-66-3	61	i, j, k, n, †	100 µl, B
Tetrahydrofuran (THF)	109-99-9	67	d, n	100 µl, A
Vinyl acetate	108-95-4	72	d*, i, j, m, n	100 µl, A
Ethyl acetate	141-78-6	77	d*, i, n	100 µl, A
Ethanol	64-17-5	78	d*	200 µl, B

[¶] see Table 2-1 for key to lists of chemicals

* currently identified as a VVOC and no LCI value assigned (AgBB, 2012)

† also listed as an EU Category 1A or 1B carcinogen (EGDS, 2012)

Following equilibration the bag outlet was attached to two Tenax TA tubes or two multi-sorbent tubes connected in series with a brass union (alternatively a tee fitting was used to enable simultaneous sampling both through two Tenax TA tubes and two multi-sorbent tubes). Air was drawn through the tubes using a Casella TUFF™ Plus personal sampling pump (with low flow adaptor) at a flow rate of between 40 and 200 ml min^{-1}.

The experimental set up for the bag experiments is shown in Plate 5-3. A total of 34 bags were prepared with volumes between 3 and 26 litres to allow a range of air sample volumes between 0.2 and 10 litres to be tested. The temperature of the laboratory over the duration of these experiments ranged between 21 and 24 °C. For the final six bags, air with a relative humidity of 50 % was used in order to check the effect of a humid atmosphere on breakthrough. Sampled tubes were stored at room temperature and analysed within one week on the TD-100/GC/MSD system. The analytical procedure was as described in Appendix A.5, except that multi-sorbent tubes rather than Tenax TA only tubes were used to calibrate for the VVOCs investigated (because of concern about the possibility of breakthrough of VVOCs on Tenax TA during spiking).

Plate 5-3 Experimental set up for Nalophan bag tests of VVOCs using duplicate sampling

5.2.2.2 SVOC atmosphere - DEHT in FLEC/μ-CTE

A source of DEHT was formed by placing the FLEC over the recovery test kit (see Appendix A.3.8) to which DEHT had been added. Air of 50 %RH and a flow rate of about 200 ml min^{-1} was passed through the FLEC. Periodic sampling was undertaken from the FLEC air outlet over a 2 week period using Tenax TA sorbent and air volumes of between 1 and 75 litres. During a third week the flow rate through the FLEC was increased to around 400 ml min^{-1} and duplicate sampling onto the two sorbent types was undertaken using air volumes of 150-300 litres. In order to increase the emission rate of DEHT, a second source was created by adding 8 ml of the neat chemical into a 10.5 cm diameter petri dish which was placed in the carpet test plate and covered with the FLEC. Periodic sampling onto both sorbent types was undertaken over a 10 day period with air volumes of around 200 litres.

For the μ-CTE, a third source of DEHT was prepared by adding 2 ml of the chemical to a vial of diameter 25 mm. The source was placed in one of the micro-chambers and the instrument was equilibrated at 50 ºC for 1 hour with an air flow of 100 ml min^{-1}. A Tenax TA tube was attached to the outlet of the chamber for 1 hour to give a sample volume of six litres. During a second run with the μ-CTE, the instrument was equilibrated at 50 ºC for 3 hours, then duplicate sampling was undertaken over a 5 hour period onto both sorbent types at a flow rate of 40 ml min^{-1} through each tube (to give a sample volume 12 litres). Three further runs were undertaken using the same conditions, except that the μ-CTE was heated to 100 ºC. Sampled tubes were analysed on the TD-100/GC/MSD system using the procedure developed for the determination of DEHT.

5.2.3 Determination of formaldehyde using TD

The reference (acetylacetone) method was applied to aid the establishment of a suitable source of formaldehyde. For this the FLEC was set up over a glass desiccator, as had been used with the foam sealant (Section 5.2.1.2), and a flow rate of about 250 ml min^{-1} of 50 %RH air was passed through the system. A control sample of the air exiting the FLEC was first undertaken by connecting two gas washing bottles containing deionised water to an empty steel tube attached to the FLEC air outlet and

drawing air through the gas washing bottles at a rate of 200 ml min^{-1} for 150 minutes (30 litres air) using a Cassella TUFF air sampling pump. Analysis involved heating a portion of the gas washing water, together with solutions of acetylacetone and ammonium acetate, followed by determination of the fluorescence intensity of the resulting solution. Full details of the method are given in Appendix A.7. A range of plywood/MDF materials cut into strips were placed in the desiccator and tested in turn by sampling the outlet air after 24 hours. An appropriate concentration of formaldehyde (~ 0.10-0.15 mg m^{-3}) was obtained with a plywood material, so the flow of air over this material was maintained to allow trialling of the 2-hydroxymethylpiperidine (2-HMP) method.

The plan for the 2-HMP method was to build on the work of Veasey (2000) which had investigated the impregnation of the reagent onto a filter placed at the front of the sorbent tube. 2-HMP reacts with formaldehyde in the air being sampled to form a volatile product, formaldehyde oxazolidine (FO) which passes onto the sorbent bed. 2-HMP is, however, itself fairly volatile and will to a certain extent also be drawn from the filter onto the sorbent, so it is necessary to check the separation of the 2-HMP reagent from FO. 1 µl aliquots of a solution of 2-HMP in dichloromethane (3,100 µg ml^{-1}) and of a commercially obtained solution of FO in toluene at a concentration of 2,000 µg ml^{-1} (Supelco, Dorset) were spiked onto conditioned Tenax tubes, purged with a helium flow of 100 ml min^{-1} for three minutes and used to establish TD-100/GC/MSD conditions for this analysis. Primary desorption temperatures of 200 °C, 250 °C and 280 °C were investigated and no advantage was found for selection of the higher temperatures i.e. a very small amount of carry-over was observed on the tube using 200 °C and this did not decrease with the use of a higher temperature. A primary desorption temperature of 200 °C was therefore applied. 200 °C was also used as the cold trap high temperature and the flow path was set at 150 °C, while other TD settings were the same as for VOC analyses (see Appendix A.5). The following GC oven programme was found to separate the two compounds and elute contaminants present in the samples: 50 °C for 1 minute, 2 °C/min to 120 °C, 20 °C/min to 280 °C, hold for 5 minutes (49 minute run). A solvent delay of 12 minutes was set to mask the elution of the dichloromethane and toluene.

A compound was required to act as an internal standard for this method to correct for fluctuations in detector response, as in the use of d8-toluene for VOC analyses (see Section 2.5.2). Due to its close elution to toluene which is present as a solvent for the FO standard, another compound needs to be selected which will elute after toluene but before FO and 2-HMP. The ideal compound would be similar to FO, perhaps a deuterated version of the compound. For these preliminary trials, however, diacetone alcohol was selected as it is a compound of moderate polarity, has an appropriate boiling point, is unlikely to be present in the emissions from wood based materials and was readily available. A solution of this compound was prepared in methanol at a concentration of 100 ng μl^{-1}. The MSD was set to record in full scan mode with an extracted ion of mass 97 being used to quantify FO. A calibration was undertaken for this compound by diluting two vials of the stock solution by different amounts in methanol to give formaldehyde equivalent amounts of between 18 and 460 ng μl^{-1}. 1 - 2 µl aliquots of these solutions were spiked onto conditioned Tenax TA tubes, together with 0.5 µl of the internal standard solution. The methanol was purged from the tubes (helium flow of 100 ml min^{-1} for 3 minutes) and they were analysed using the TD-100/GC/MSD.

The empty tube in the FLEC air outlet was replaced with a conditioned Tenax TA tube and the rear of this was connected to the two gas washing bottles containing fresh deionised water. A 30 litre sample of air was drawn through the system after which the sorbent tube was analysed using the TD-100/GC/MSD and the contents of the gas washing bottles analysed using the acetylacetone method. This experiment was repeated once with a fresh Tenax TA tube, fresh water and a 5.1 mm sintered PTFE filter (Markes part no. U-DISK1) inserted into the front end of the sorbent tube and a second time with additionally 1 µl of the 2-HMP solution injected onto a fresh filter. The solvent was allowed to evaporate before the filter was inserted into the mouth of the tube. The filters were removed from the tube prior to analysis.

Further experiments were undertaken to investigate the effect of a number of variables as follows:

1) Increased volume of 2-HMP solution spiked onto a filter. For this a solution of 2-HMP in methanol was prepared in place of the dichloromethane (to avoid overloading the analytical system with solvent)
2) use of a 6.5 mm sintered PTFE filter (Markes part no. U-DISK3) for spiking the reagent onto (this proved easier to use as it could be inserted behind a gauze cap routinely used with these sorbent tubes for diffusive sampling)
3) reduction of the air flow through the samplers (the flow into the FLEC was reduced to 100 ml min^{-1} and that through the samplers to 50 ml min^{-1})
4) using glass Tenax TA tubes in place of stainless steel tubes [as recommended by Thomas, (2010)]
5) test of multiple spiked filters (the recovery of FO obtained using three spiked filters inserted into the gauze cap was compared to that obtained using one filter).

Use of the larger filter size and gauze cap required an empty tube to be connected to the FLEC outlet then the cap and tube to be connected to the back of this using a short length of plastic tubing. The experimental set up for this adaptation, including the gas washing bottles containing water for the acetylacetone method, is shown in Plate 5-4.

The following background/control tests were also undertaken:

1) spiking the 2-HMP in methanol solution into Tenax TA tubes with purging of the methanol before analysis
2) addition of methanol to used filters then injection of the solution into Tenax TA tubes
3) sampling from an empty desiccator using the 2-HMP method.

Plate 5-4 Plywood sample being tested using the FLEC with analysis for formaldehyde using the 2-HMP and the acetylacetone methods

5.3 Results and Discussion

5.3.1 Emission tests using two sorbents

5.3.1.1 Composite door foam – source of VVOCs

The composite door sample had previously been investigated as part of the study of screening tests (Chapter 3). Testing of different portions of the product separately had shown the foam to be the source of the VVOCs n-pentane and methylcyclobutane (MCB) and the GRP to be the source of a range of VOCs dominated by styrene, xylenes and butyl acetate. Foam which had been in contact with the GRP was found to be a secondary source of these VOCs. Chromatograms obtained in the present study from analysis of Tenax TA tubes which had been used in series to take a 4.6 litre air sample of the emissions from a portion of foam are shown in Figure 5-2(a). Corresponding chromatograms from analysis of the MS1 tubes which had been used simultaneously to sample from the µ-CTE are shown in Figure 5-2(b). The first in line multi-sorbent tube is seen to trap greater amounts of the VVOCs than found on the first in line Tenax TA tube, whereas amounts of the VOCs were similar on the two tubes. N-pentane and MCB

show significant breakthrough to the second in line Tenax TA tube, but no detectable amounts of these two compounds were found in the second in line multi-sorbent tube. For the less volatile compounds neither sorbent showed any breakthrough to the second tube using a sample volume of 4.6 litres.

Concentrations of compounds emitted from the portions of foam and trapped by nine pairs of Tenax TA and multi-sorbent tubes that had an air sample volume of 0.75 litres were determined. Sixteen compounds were observed in quantifiable amounts in at least five of these pairs of tubes. Mean concentrations recorded for the pairs of samples with quantifiable amounts of eight dominant compounds are shown in Figure 5-3(a). These concentrations were compared using paired t-tests (P = 0.05) and the difference was found to be statistically significant for n-pentane and MCB and not significant for any of the less volatile compounds. Details of the statistical analysis are given in Table E-1 (Appendix E). Mean concentrations of compounds emitted in smaller amounts from the foam are shown in Figure 5-3(b), with details of the statistical analysis contained in Table E-2. These compounds would all be categorised as VOCs, the most volatile being methyl isobutyl ketone (MIBK) which has a boiling point of 117 °C.

The only statistically significant difference in the concentrations of these compounds was found for 1-methoxy-2-propylacetate; where the concentration using Tenax TA was found to be significantly higher than that for the multi-sorbent tubes, but the magnitude of this difference was small (the mean of the % differences between each pair was 3.5 %).

Benzene-acetaldehyde showed a higher mean concentration on the multi-sorbent tubes than on Tenax TA and epoxyethylbenzene showed a higher mean concentration on Tenax TA than on the multi-sorbent tubes, though these differences were not found to be statistically significant due to the variability within the results. These two compounds had been identified only using the NIST library and quantified using the response factor for toluene, so their performance on these sorbents would ideally be investigated further using pure standard materials. The highest boiling compound found from this material was benzoic acid, which has a boiling point of 249 °C, and this showed comparable amounts using the two sorbent types.

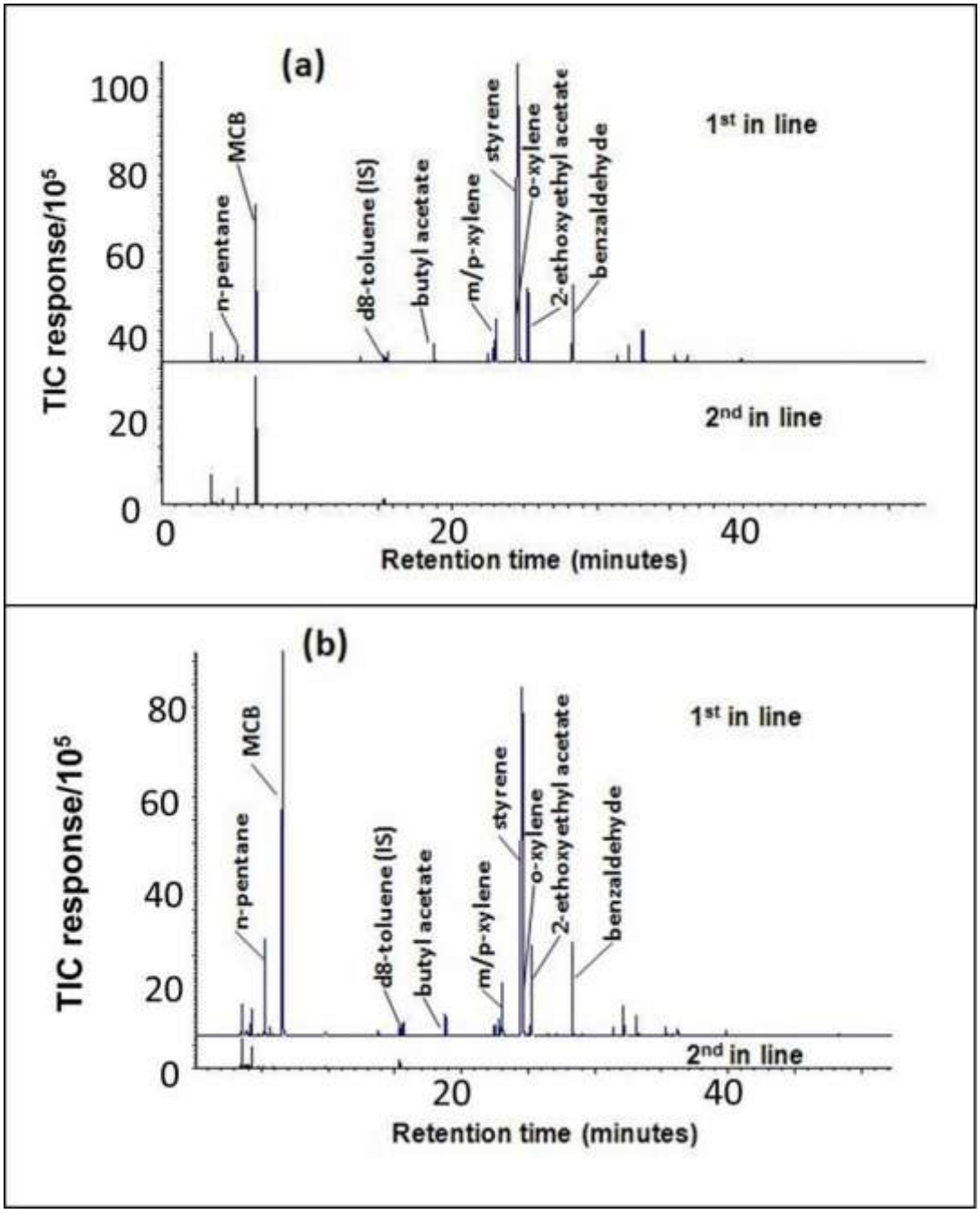

Figure 5-2 Chromatograms of emissions from PU foam from composite door tested in μ-CTE with 4.6 litres air sampled through (a) Tenax TA tubes and (b) MS1 tubes

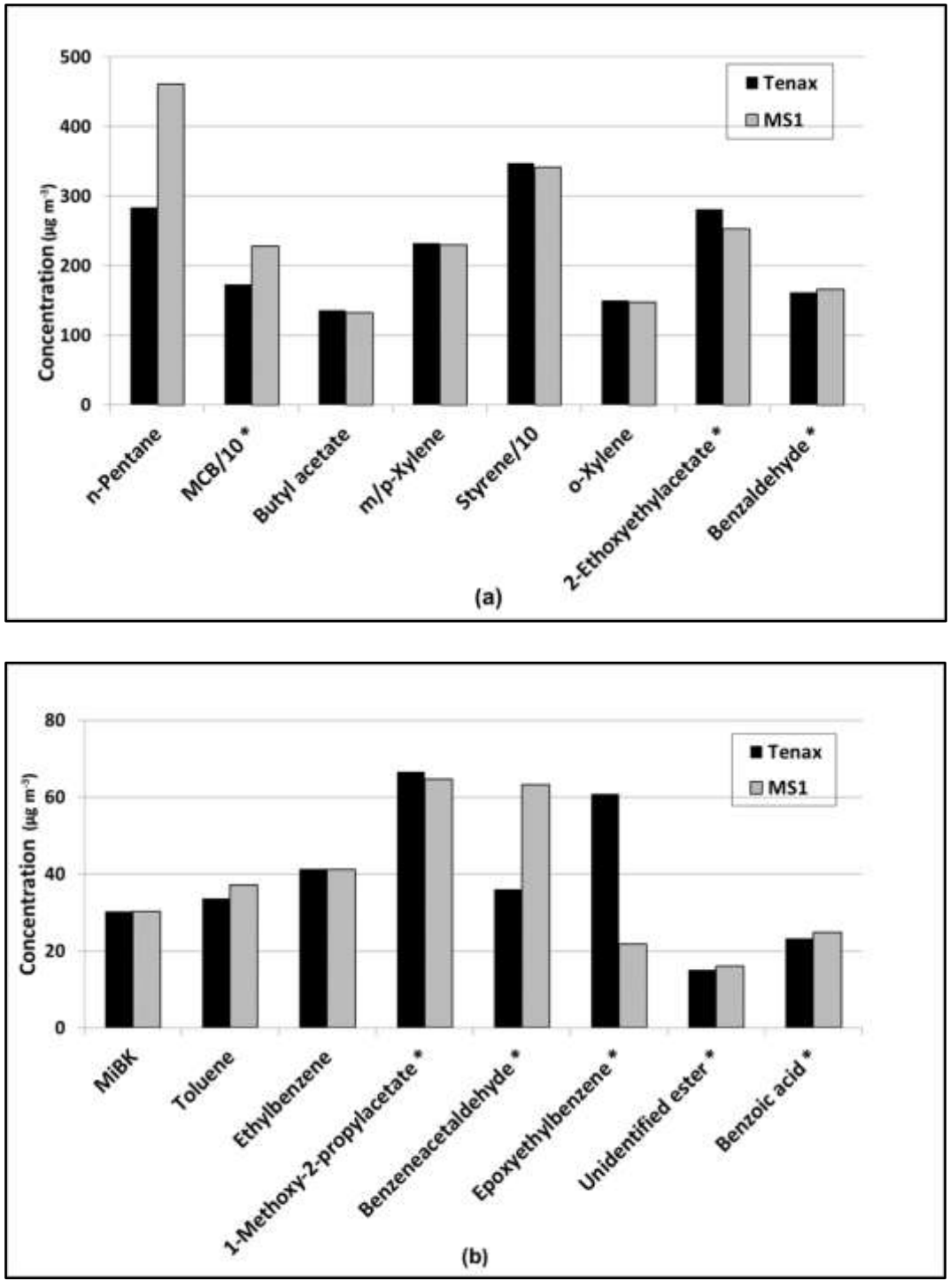

Figure 5-3 Mean concentrations of VVOCs and VOCs emitted from PU foam from a composite door tested in µ-CTE and sampled onto Tenax TA and MS1 (a) dominant compounds (b) compounds detected in smaller amounts

(* denotes no pure standard available to confirm identity, quantified using response factor for toluene)

5.3.1.2 Foam sealant – source of VVOCs

The safety data sheet for the foam sealant tested listed methylenediphenyl diisocyanate (MDI), isobutane, dimethyl ether and propane as ingredients. The freshly sprayed material was found to release considerable amounts of dimethyl ether, isobutane and n-butane. Smaller amounts of a range of higher boiling compounds (dominated by several siloxanes) were also found. Propane (boiling point -42 °C) would not be expected to be trapped by either of the tube types tested and MDI, which boils at 314 °C, is a particularly difficult compound to determine, requiring a specific sampling and analysis procedure (Widdowson, 2012). Figure 5-4 shows a chromatogram obtained from analysis of a multi-sorbent tube which had been used to sample immediately after spraying and placing the material under the FLEC. Isobutane and n-butane were still being released from the material in significant amounts by the 25th day of sampling, while the majority of the other compounds were no longer detectable by this time (Figure 5-5).

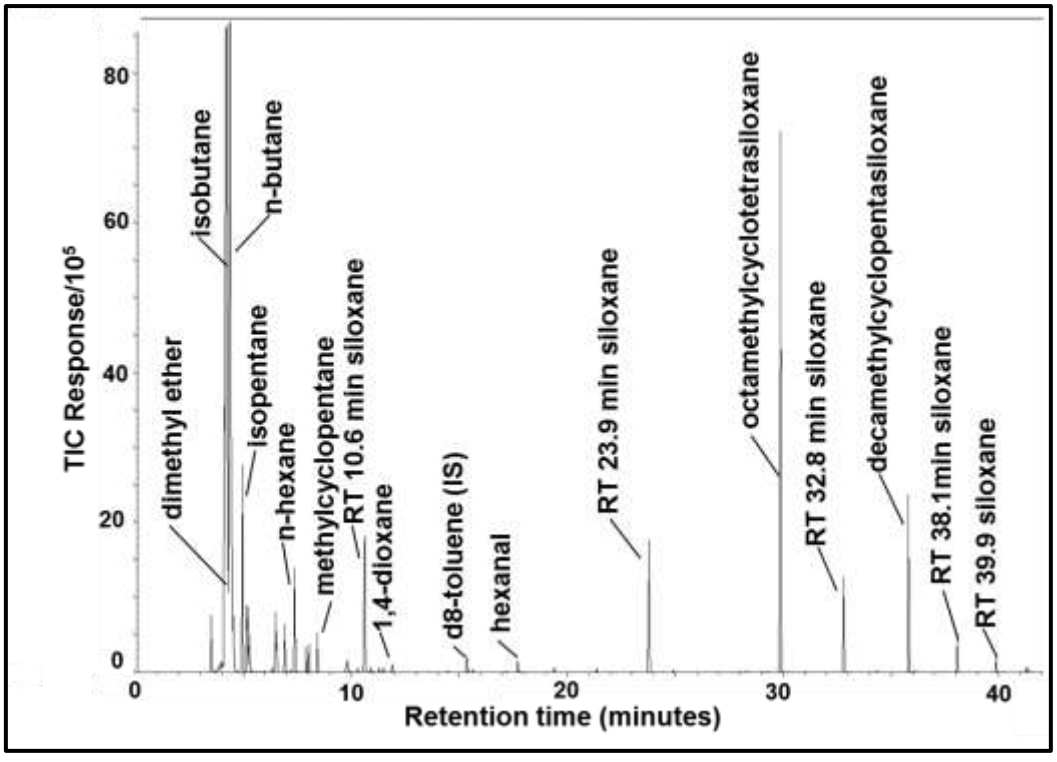

Figure 5-4 Chromatogram of emissions from foam sealant tested using FLEC and sampled using a multi-sorbent tube

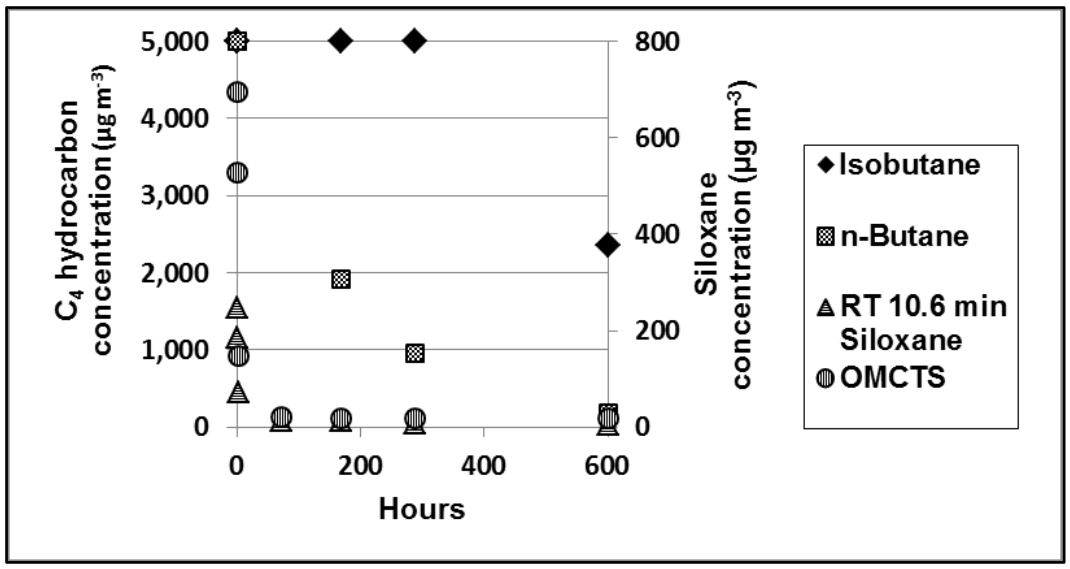

Figure 5-5 Approximate concentrations of two C_4 hydrocarbons and two siloxanes released from foam sealant placed under FLEC

(all compounds quantified as toluene and values above 5,000 µg m^{-3} set at this value)

Eleven pairs of Tenax TA and multi-sorbent tubes were used to sample the emissions from the material over the 25 day test period using a sample volume of 0.5-1.5 litres and 18 compounds were observed in quantifiable amounts in at least six of these pairs of tubes. Mean concentrations recorded for the pairs of samples with quantifiable amounts of the nine most dominant compounds are shown in Figure 5-6(a) with concentrations of compounds emitted in smaller amounts being shown in Figure 5-6(b). Details of the statistical analysis are given in Table E-3 and Table E-4. Concentrations of isobutane and n-butane determined using the multi-sorbent tubes were found to be significantly greater than those found with Tenax TA (paired t-tests, $P = 0.05$). For dimethyl ether a higher mean concentration was recorded using Tenax TA, though the difference was not found to be statistically significant. Results for this compound were very variable and, given its volatility (boiling point -24 °C), it is likely that neither Tenax TA nor the multi-sorbent tube are trapping it effectively.

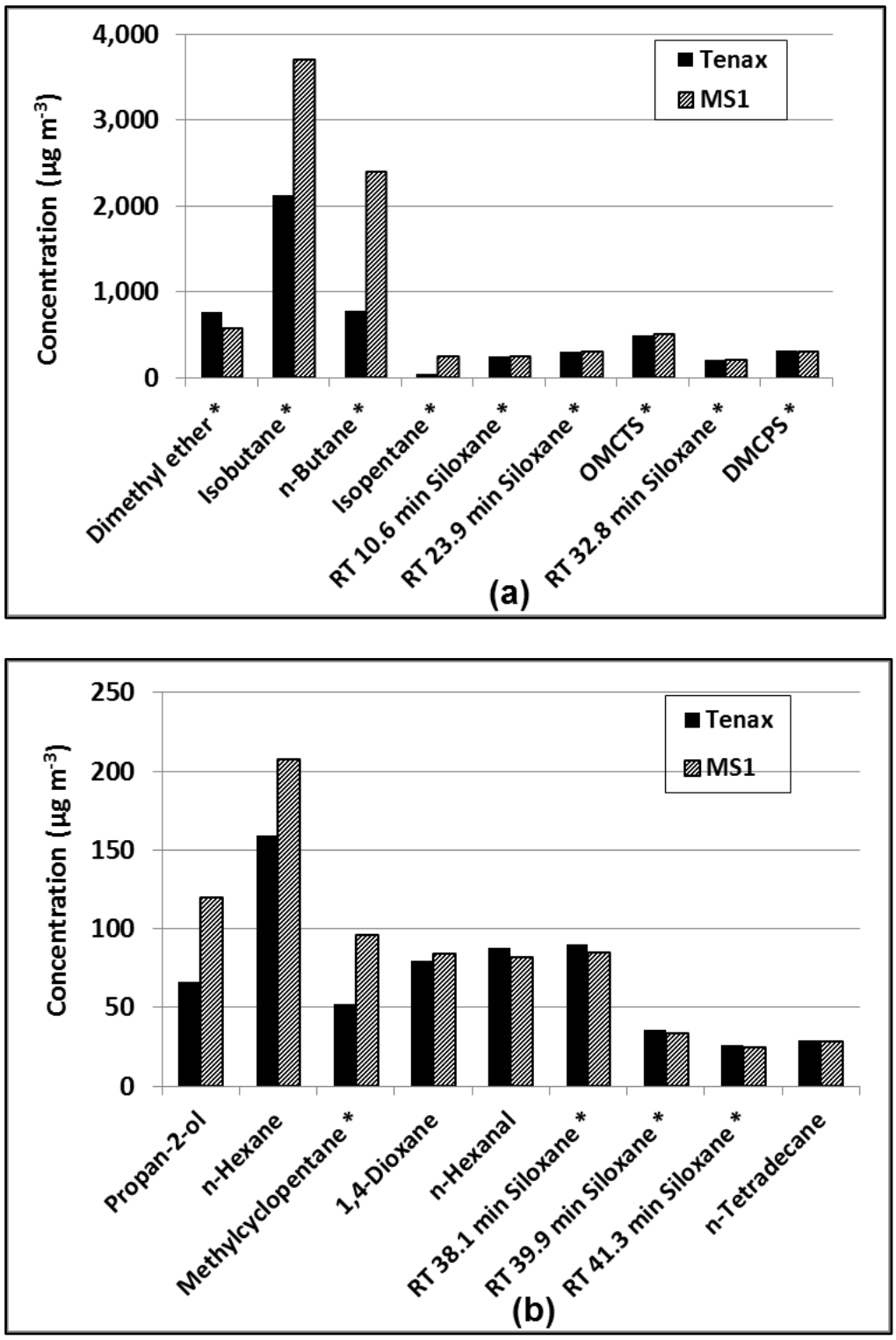

Figure 5-6 Mean concentrations of VVOCs and VOCs emitted from foam sealant tested using FLEC and sampled onto Tenax TA and MS1 (a) dominant compounds (b) compounds detected in smaller amounts

(* denotes no pure standard available to confirm identity, quantified using response factor for toluene)

Four other compounds all showed differences in the concentrations determined using the two sorbent types. Isopentane (boiling point 27 °C), propan-2-ol (boiling point 82 °C), n-hexane (boiling point 69 °C) and methylcyclopentane (boiling point 72 °C) were all found in greater amounts using MS1 than using Tenax TA, though these differences were not found to be statistically significant. When the concentrations obtained from eight pairs of tubes which were used to sample emissions from the foam using a sample volume of between 1.5 and 5.0 litres were compared, the difference was found to be statistically significant for propan-2-ol, and nearly significant for the other three of these compounds (Table E-5). This is probably due to the sampling volume being either close to or exceeding the breakthrough volume of these compounds on Tenax TA. Other compounds present in the emissions from the foam sealant were found to show comparable concentrations using both sorbent types for all sample volumes up to 5 litres. These compounds are all VOCs and cover the boiling point range of 101 °C (1,4-dioxane) to 254 °C (n-tetradecane).

The tubes which had been connected in series behind the sampling tubes were examined for the presence of the 18 compounds observed in detectable amounts from the foam sealant. Neither the Tenax TA nor the multi-sorbent tubes contained any presence of 1,4-dioxane, n-hexanal, n-tetradecane or any of the siloxanes, with the exception of that occurring at a retention time of 10.6 minutes (tentatively identified as hexamethyl disiloxane). This compound had been detected in seven of the 12 pairs of air samples for which back up tubes had been employed and breakthrough was observed for four of the Tenax TA tubes and none of the multi-sorbent tubes. The amount found in the second in line tube in these instances was between 29 and 82 % of that found on the first in line tubes. Breakthrough information for this and the other compounds which showed some breakthrough in one or more tubes is summarised in Table 5-2.

As expected, dimethyl ether showed considerable breakthrough in all samples on which it was detected for both Tenax TA and multi-sorbent tubes, confirming that neither sorbent is effective for this compound. Isobutane and n-butane showed significant breakthrough in all samples using Tenax TA. However the very high concentrations of these two compounds recorded on some of the tubes suggests that these results may be subject to possible overloading of the sorbent. With the multi-sorbent tube,

breakthrough was observed in all of the samples for isobutane and in five of the samples for n-butane, and for both of these compounds the % breakthrough values covered a wider range than had been found using Tenax TA. Further tests were therefore undertaken for these two compounds using the µ-CTE (see below). The other four compounds which had been found in higher amounts on the multi-sorbent tubes than on Tenax TA showed breakthrough in all the Tenax TA tubes, with the exception of n-hexane which only showed breakthrough for the highest sample volume used (2.6 litres) and methylcyclopentane which showed no breakthrough up to a sample volume of 2.6 litres, though the amounts found in the first in line tubes were low (<30 ng).

Table 5-2 Compounds found in emissions from foam sealant and for which some breakthrough was observed (sampling onto two tubes of the same sorbent type connected in series)

Compound	Number of the 12 samples in which a detectable amount found	Tenax TA		MS1	
		Number showing breakthrough	Range of % breakthrough	Number showing breakthrough	Range of % breakthrough
Dimethyl ether	7	7	64 – >100 %	7	32 – >100 %
Isobutane	12	12	70 – >100 % *	12	0.2 – >100 % *
n-Butane	12	12	60 – >100 % *	5	7 – >100 % *
Isopentane	5	5	62 – 95 %	0	---
Propan-2-ol	10	10	32 – 100 %	6	4 – 30 %
n-Hexane	3	1	42 %	0	---
RT10.6 min siloxane	7	4	29 – 82 %	0	---

* Amounts found above calibration limit for some samples so could be subject to error

For the multi-sorbent tube, no breakthrough was observed for isopentane, n-hexane or methylcyclopentane, whereas some presence of propan-2-ol was found on the back up tube in six of the 10 samples in which this compound was detected. In each of these cases the breakthrough was lower than that found using Tenax TA alone, with a

maximum value of 30 % of that found on the first in series tube being recorded, compared to 100 % for Tenax TA. For amounts on the first tubes of greater than 62 ng, less than 10 % breakthrough was observed. A breakthrough of 10 % for a particular compound has been suggested as the cut-off point for regarding data for the compound as reliable (Markes, 2012). The multi-sorbent tube is therefore showing significant improvement in performance for these four compounds over that shown by Tenax TA alone.

To investigate the extent of improvement in performance of the multi-sorbent tube over Tenax TA for the C_4 hydrocarbons, further samples were taken from a portion of the sealant material placed in the µ-CTE. This test gave emissions of n-butane and isobutane which were at a more appropriate level, with none of the other compounds being observed. Figure 5-7 shows the percentage breakthrough for these two compounds using Tenax TA and multi-sorbent tubes. For both compounds significant breakthrough was observed for Tenax TA from the smallest sample volume (200 ml). Using the multi-sorbent tubes no breakthrough was observed for isobutane (boiling point -10 °C) below a sample volume of 3 litres, while above this volume there was a steady increase in percentage breakthrough with increasing sample volume. For n-butane (boiling point -0.5 °C) no breakthrough was observed below a sample volume of 5 litres, with some breakthrough being observed for three of the five samples on which the compound was detected above this volume. These findings are consistent with work by HSE which found a breakthrough volume of around 10 litres for the related compound 1,3-butadiene (boiling point -4 °C) using a tube fully packed with Carbograph 5TD (HSE, 2003).

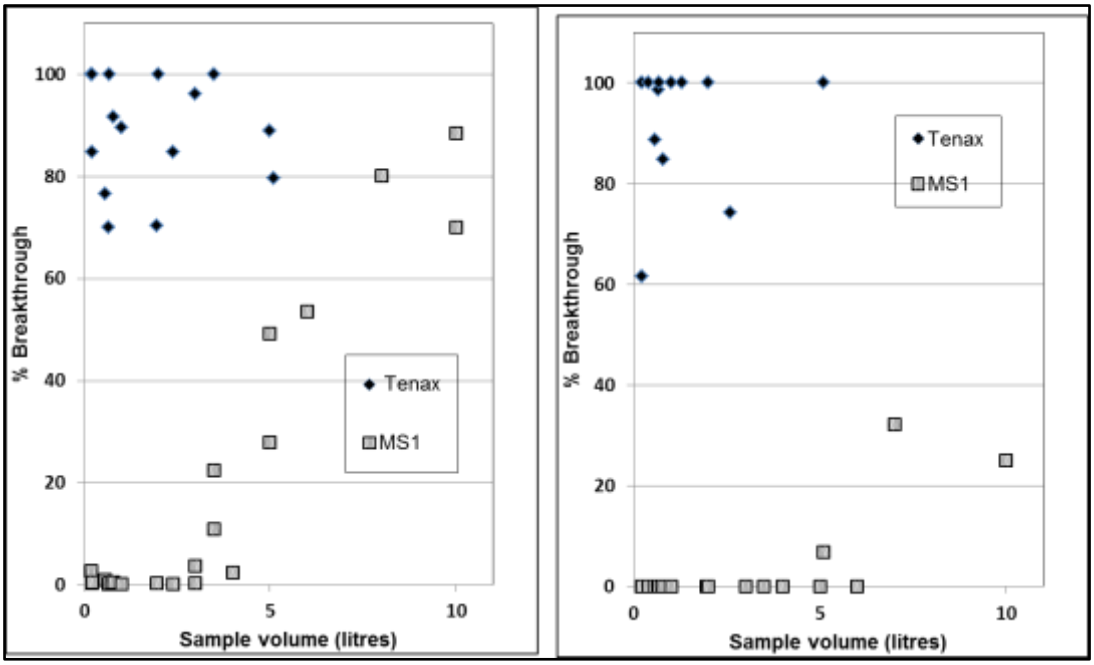

Figure 5-7 Breakthrough of (a) isobutane and (b) n-butane emitted from foam sealant using two sorbent tubes connected in series

5.3.1.3 Wall covering – source of SVOCs

Analysis of the two chemicals used as plasticisers in the wall covering materials gave a sharp peak at a retention time of 58.1 minutes, with dominant ions with mass to charge ratios (m/z) 149, 261, 112, 279 and 167, which was identified as DEHT. A range of smaller peaks, with retention times between 57 and 61 minutes and dominant ions of m/z 149, 167, 293, 127 and 57, were also observed. This group of peaks resulted from the DINP standard which was stated to be of technical grade and containing a mixture of isomers. Previous studies involving determination of DINP (Nagorka et al., 2011; Schossler et al., 2011), had found a similar pattern of peaks, resulting in an increased effort being required to quantify this compound. Using the modified GC method the retention time of DEHT was reduced to 33.6 minutes and the retention time range for the DINP isomers was 33-37 minutes. The following ions were set up in the SIM ionisation mode MSD method; 0-20 minutes, m/z 98 and 100 (for d8-toluene, internal standard); 20-41 minutes, m/z 261 (for DEHT), m/z 293 (for DINP), m/z 149 and 167 (for both compounds).

Neither of these two compounds was observed in the emissions from the wall covering up to day 18 of the test, where sample volumes of between 10 and 50 litres and analysis

using the SIM method were used. The larger volume samples also showed no presence of DINP, but DEHT was observed in these, results of which are given in Table 5-3. Comparison was undertaken by normalising the area of the DEHT peak to that of the internal standard. These samples each used a flow rate of around 230 ml min^{-1} and a sampling time of 24 hours. The material was therefore being found to be a source of DEHT emissions, but, due to the low rate of emission, an excessively long sampling time was required to achieve a detectable result on a single tube. The emission of semi-volatile organic compounds from this material would be expected to increase gradually over an equilibration period and then to be fairly stable over time. A rather more volatile compound emitted from this material, TXIB, was found to reach a steady-state concentration after about 1 day (Section 3.3.3). DEHP and DINP have been found to take around 50 days to reach steady-state concentration using a FLEC (Schossler et al., 2011). The results obtained in the present study give a suggestion of a slight increase in amount between 20 and 26 days, which makes any potential difference in performance between the two sorbents difficult to observe. For a reliable comparison of uptake on different sorbents duplicate sampling would be preferred. Use of a higher flow rate would simply dilute the emitted DEHT and a longer sampling time could exacerbate risks of drift in flow rates occurring with the sampling pumps. Further experiments therefore investigated the use of liquid DEHT to compare the uptake on Tenax and the multi-sorbent tube.

Table 5-3 Amount of DEHT emitted from a wall covering using the FLEC

Time since material placed under FLEC (days)	Sample volume (l)	Sorbent	MSD mode	Peak area		Normalised DEHT area (%)
				d8-toluene (IS) (m/z 98)	DEHT (m/z 261)	
20	320	Tenax	SIM	5,623,670	137,115	2.4
24	330	MS1	SIM	4,735,847	136,733	2.9
25	330	Tenax	FS	2,134,213	63,596	3.0
26	335	MS1	FS	2,250,086	73,401	3.3

5.3.2 Tests of VVOC/SVOC atmospheres

5.3.2.1 VVOC atmosphere – using Nalophan bags

Some trialling of the bag volume and VVOC amounts was required to obtain loadings on the tubes within the calibration ranges for each compound being tested (approximately 2-2,000 ng on the tube, but varying due to differences in MS response for different compounds). Breakthrough values were only regarded as valid if the amount found on the first in line tube was above 100 ng (otherwise low levels of breakthrough would be undetectable). An exception to this was in the case of high % breakthrough which was observed at a lower loading level. Also values above the top of the calibration range for a first in line tube were excluded unless no presence of the compound was detected in the corresponding second in line tube.

The percentage breakthrough occurring at different sample volumes on the two tube types for six of the VVOCs tested are shown in Figure 5-8. For MTBE, Figure 5-8(a), breakthrough with Tenax TA occurred from the smallest sample volume tested (200 ml), whereas no breakthrough for any sample volume up to 10 litres was observed with the multi-sorbent tubes. Isoprene, Figure 5-8(b), showed breakthrough of less than 10 % on Tenax TA up to a sample volume of 400 ml, but breakthrough above this volume increased steadily reaching 80 % for a sample volume of 5 litres, whereas again no breakthrough occurred over the range of volumes tested for the multi-sorbent tubes.

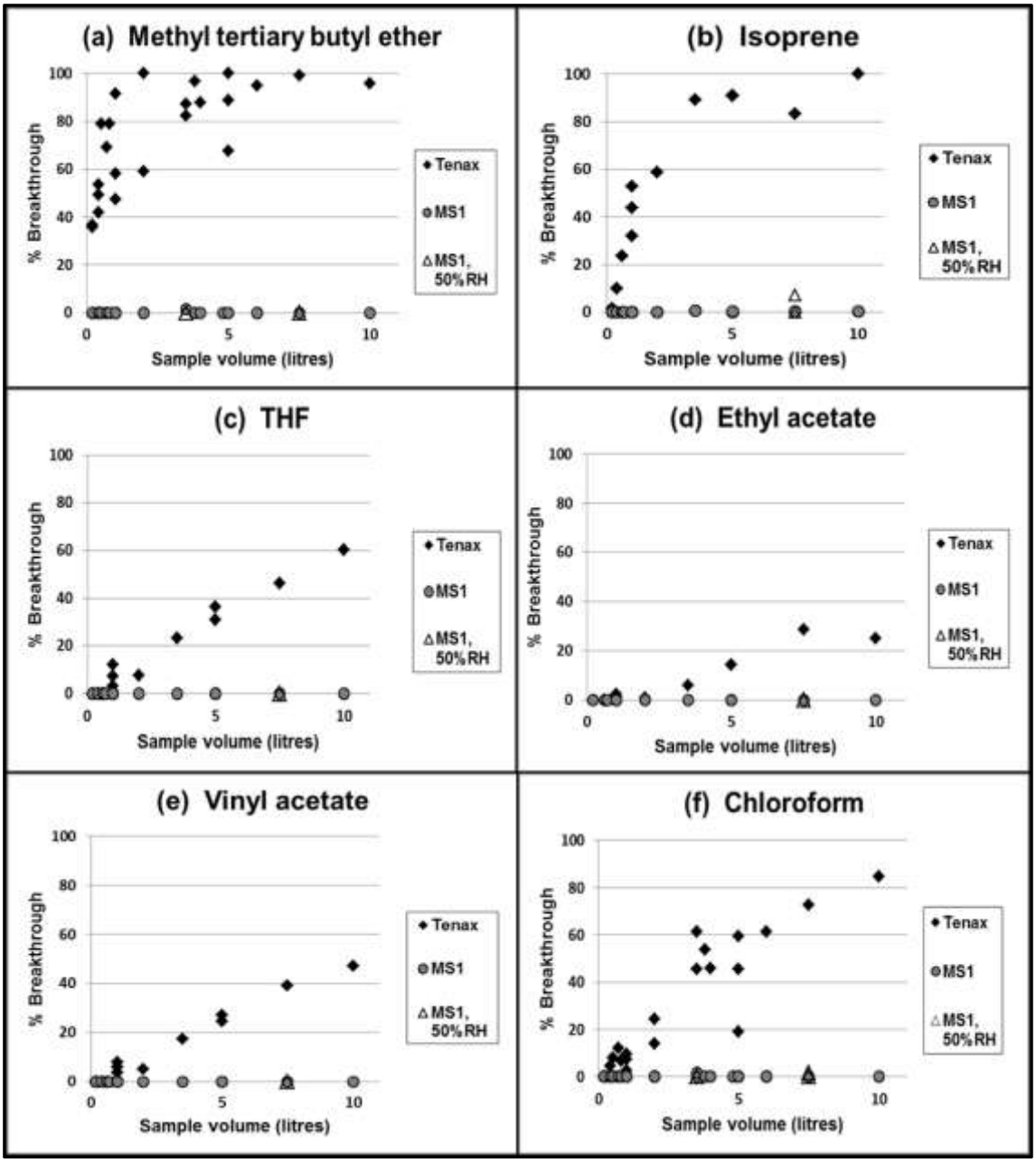

Figure 5-8 Breakthrough of six VVOCs using two sorbent tubes, connected in series, to sample from an atmosphere of these compounds contained within a Nalophan bag

In all, six of the 10 compounds tested showed no breakthrough up to a sample volume of 10 litres with the multi-sorbent tubes, in contrast to their performance with Tenax TA. These also included THF, Figure 5-8(c) and ethyl acetate, Figure 5-8(d), which showed breakthrough on Tenax TA of around 35 % and 15 % respectively for a sample volume of 5 litres, and vinyl acetate Figure 5-8(e) and chloroform Figure 5-8(f) which

gave similar results, with around 25 % and 50 % breakthrough, respectively, on Tenax TA for a sample volume of 5 litres. Figure 5-9 shows the results for the remaining four compounds tested. For acetone, Figure 5-9(a), breakthrough of about 10 % occurred with a sample volume of 400 ml on Tenax TA, whereas with the multi-sorbent tubes about 4 litres could be sampled before this level of breakthrough occurred. Dichloromethane (DCM) gave similar results, Figure 5-9(b), with only 200 ml through Tenax TA tubes having a breakthrough of <10 %, whereas on MS1 this was increased to 1 litre. For ethanol, Figure 5-9(c), all sampling volumes gave breakthrough of >10 % using Tenax TA, with the multi-sorbent tubes offering marginal improvement of up to 500 ml before breakthrough exceeded this level. Only acetaldehyde, Figure 5-9(d), showed no improvement from use of the multi-sorbent tubes, with breakthrough for both sorbent types exceeding 10 % with a sample volume of 200 ml.

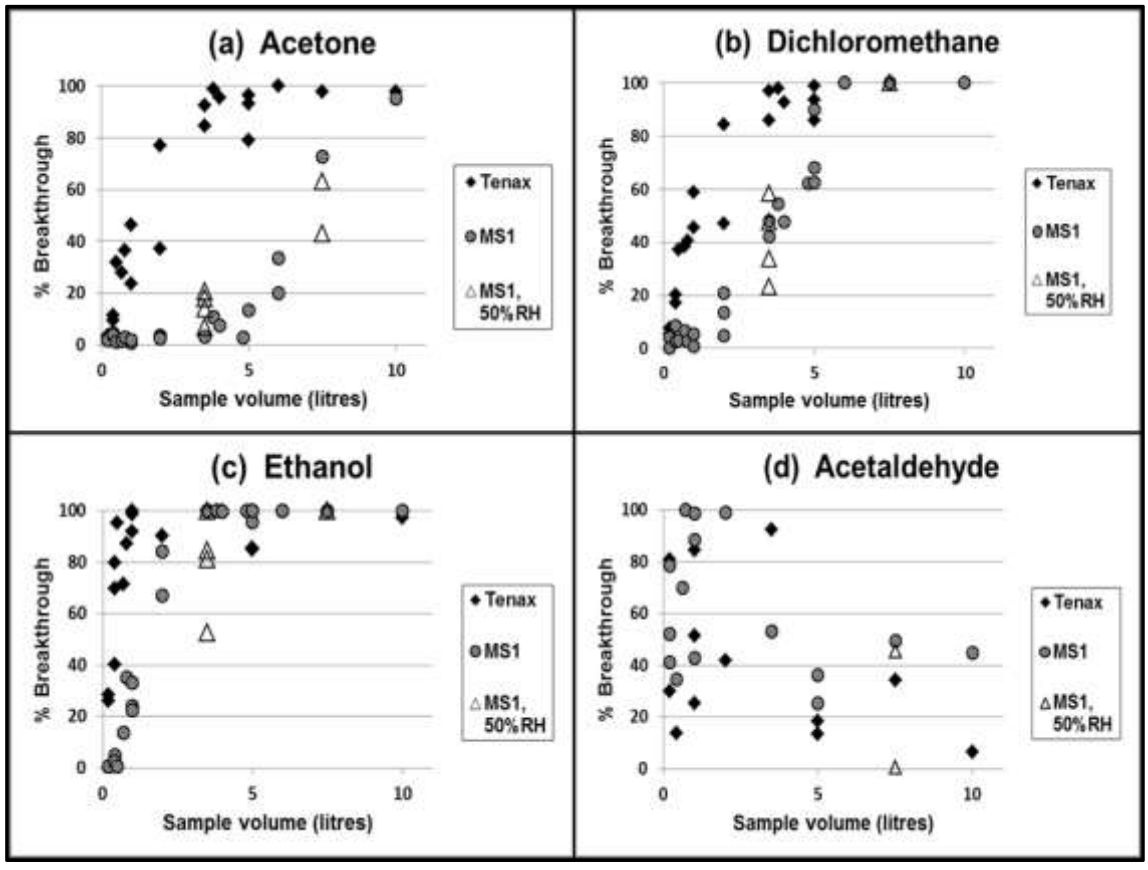

Figure 5-9 Breakthrough of a further four VVOCs using two sorbent tubes, connected in series, to sample from an atmosphere of these compounds contained within a Nalophan bag

In the bag experiments using humidified air, a sample volume of 7.5 litres passed through multi-sorbent tubes was tested for all compounds and tests were also undertaken using a volume of 3.5 litres for five of the compounds. No effect of humidity was found for the six compounds which had shown no breakthrough up to a sample volume of 10 litres using the multi-sorbent tubes, i.e. no breakthrough was found using 7.5 litres of air with a relative humidity of 50 %. For acetone, four tests with 3.5 litres of air resulted in % breakthrough values ranging between 7-20 %, which was slightly higher than had been found for this sample volume with dry air (3-10 %). So, although this compound definitely shows an improved breakthrough volume using the multi-sorbent tubes, further tests in a humid atmosphere would be needed to confirm the maximum sample volume which reliably gives a % breakthrough of <10 %. For DCM the breakthrough with 3.5 litres of humid air (about 40 %) was similar to that which had occurred with this volume of dry air. This suggests that breakthrough up to 1 litre will not be affected for this compound either, but again further tests would be required to confirm this.

Recovery of two of these compounds, DCM and chloroform, was investigated in a study into the performance of a number of sorbents by Brown and Shirey (2001). The results obtained for DCM in the present study are consistent with those of the previous study, using a tube fully packed with the graphitised carbon Carbopack X, where >80 % recovery was found for volumes up to 1 litre and between 20 and 80 % recovery for a volume of 5 litres. For chloroform, the previous study found a recovery of between 20 and 80 % for all volumes tested up to 20 litres using Carbopack X, suggesting either some breakthrough or the analyte was too strongly retained by the sorbent. The present study, using the multi-sorbent tube containing some Carbograph 5TD, therefore shows better performance for this compound with no breakthrough being observed, up to the maximum sample volume tested (10 litres).

In order to increase the retention of VVOCs further, use of a carbon molecular sieve type sorbent, either instead of, or in addition to, the graphitised carbon black could be investigated. Tubes containing Tenax TA and the carbon molecular sieve Carboxen™ 569, for example, used in a study of VOCs in spacecraft air (Matney et al., 2000), found a recovery of 75 % for acetaldehyde and recoveries of 95-110 % for nine other

compounds with boiling points down to -30 °C. A further study of VOCs in the atmosphere, using tubes containing two graphitised carbons and one carbon molecular sieve, Carbotrap, Carbopack™ X and Carboxen 569, (Gallego et al., 2010) found <10 % breakthrough for DCM and acetone for a sample volume of 10 litres. (Ethanol was also investigated, but showed >10 % breakthrough for the minimum sample volume tested of 10 litres, so does not show evidence of any improvement over the sorbent combination used in the present study). One disadvantage of the use of carbon molecular sieve sorbents, however, is that they are more affected by humidity (Fastyn et al., 2005) and would require an extra step in the procedure to remove moisture from the tubes prior to thermal desorption. A further issue to be borne in mind with this type of sorbent is that it is not possible to use standards dissolved in methanol as the methanol cannot be purged off at ambient temperature and so a more complex gas phase standard introduction technique is required (Horn et al., 2007).

5.3.2.2 SVOC atmosphere - DEHT in FLEC/µ-CTE

A peak identified as DEHT was found in three of the first four samples taken from the FLEC placed over source 1 of DEHT (Table 5-4). The size of the peak did not correlate with the sample volume. The higher volume samples where duplicate sampling onto both sorbents types was undertaken (Table 5-5) showed the presence of DEHT in each case. More DEHT was recovered from the MS1 tube for the first of the pairs of duplicates and more from the Tenax tube for the second and third pairs of tubes. The reason for the sharp increase in amounts found for the third sampling period was not clear. One explanation of the variability observed could be that the analysis of this compound is proving a challenge to the analytical system and set-up. DEHT is an isomer of di-2-ethylhexyl phthalate (DEHP), which has a boiling point of 384 °C. DEHP was found to perform adequately on the system with <1 % carry-over in the system and on the tubes (Appendix C, Section C.1.4). DEHT, however, has a boiling point of 400 °C so could be more prone to sticking on either the tube or along the flow path. Significant amounts of this compound tended to be observed in empty tubes run after sample tubes, so for further studies with this compound it was decided to undertake two successive analyses of each sample tube and sum the results. This approach has been used previously (Schossler et al., 2011) for the analysis of high boiling compounds.

Table 5-4 Amount of DEHT emitted from DEHT source 1 using the FLEC

Time since source placed under FLEC (days)	Sample volume (l)	Sorbent	Peak area		Normalised DEHT area (%)
			d8-toluene (IS) (m/z 98)	DEHT (m/z 261)	
4	1.4	Tenax	4,341,626	23,908	0.5
5	12.2	Tenax	4,979,780	No peak	---
8	75.1	Tenax	5,102,767	37,512	0.7
15	42.6	Tenax	4,945,274	6,465	0.1

Table 5-5 Amount of DEHT emitted from DEHT source 1 using the FLEC and duplicate sampling

Time since source placed under FLEC (days)	Sample volume (l)	Sorbent	Peak area		Normalized DEHT area (%)
			d8-toluene (IS) (m/z 98)	DEHT (m/z 261)	
19	162	Tenax	7,054,574	57,310	0.8
	194	MS1	7,212,100	91,996	1.3
20	282	Tenax	6,201,716	128,186	2.1
	258	MS1	6,847,748	103,916	1.5
21	293	Tenax	5,179,143	582,613	11.2
	294	MS1	5,453,145	403,299	7.4

Findings for the second source of DEHT placed in the FLEC are shown in Table 5-6. These include the amounts obtained from the second desorption of the tube which ranged from 0 to 37 % of the amount obtained from the 1st desorption. The two sorbents gave similar amounts of the compound for the first 24 hour sampling period. For the second period, however, dramatically greater amounts of DEHT were recovered from the Tenax tube than from the MS1 tube. The reason for this difference could not be explained. Owing to the long sampling time (24 hours) required for these tests, further work explored the use of the µ-CTE with heating of the chamber to compare the two sorbent types.

Table 5-6 Amount of DEHT emitted from DEHT source 2 using the FLEC and duplicate sampling

Time since source placed under FLEC (days)	Sample volume (l)	Sorbent	Peak area (sum of 1st and 2nd desorption)		Normalised DEHT area (%)
			d8-toluene (IS) (m/z 98)	DEHT (m/z 261)	
6	230	Tenax	5,924,790	164,887	2.8
	236	MS1	5,423,546	188,196	3.5
10	208	Tenax	4,546,711	5,590,852	123
	204	MS1	4,494,765	595,254	13

With the μ-CTE heated to 50 °C, the initial 6 litre air sample onto Tenax from a chamber containing DEHT source 3 gave a peak which was 7.5 % of the size of the internal standard peak. This suggested that use of the μ-CTE with moderate heating would allow a speedier comparison of the performance of the two sorbent types for this chemical than was the case using the FLEC at ambient temperature. Use of the FLEC with an elevated temperature has also been reported to have been used to study emissions of an SVOC from a material, in this case DEHP from vinyl flooring (Clausen et al., 2012). Tests were undertaken at temperatures between 23 °C and 61 °C, with higher steady-state concentrations being observed, together with faster equilibrium, at the higher temperatures.

Results obtained in the present study from duplicate sampling onto both sorbent types from the μ-CTE chamber containing DEHT source 3 are given in Table 5-7. These again include the amounts found from a second desorption of the tubes which ranged from 0 to 61 % of that found from the first desorption. The test at 50 ºC gave peaks which were just 0.3 % of the size of the internal standard peak for both sorbents. The tests at 100 ºC gave significantly greater amounts of DEHT. Neither of the sorbent types was however found to give a consistently greater amount than the other. The reason for this is not clear, one explanation might be that the compound being investigated is too involatile, or 'sticky', to be determined reliably using the instrument conditions used (i.e. flow path temperature, cold trap packing and flow rates). Most methods based on sampling using Tenax TA sorbent regard n-hexadecane (C_{16}) as the top end of the volatility range to be determined. The AgBB scheme, however (see Section 1.3.3), also

requires the determination of compounds eluting within the retention range C_{16}-C_{22}, i.e. up to n-docosane which has a boiling point of 369 °C. A note in the current version of the scheme states that "the analysis of semi volatile organic compounds with an even lower volatility will encounter increasing difficulty using Tenax sampling and thermal desorption in chamber tests" (AgBB, 2012). The presence of quartz wool at the front of the multi-sorbent tube used in the present study should allow compounds of higher boiling point to be determined, but it appears that the compound selected for investigation, DEHT, may still be beyond the limits of the method using current technology.

Table 5-7 Amount of DEHT emitted from DEHT source 3 using the µ-CTE and duplicate sampling

Temperature (°C)	Sample volume (l)	Sorbent	Peak area (sum of 1st and 2nd desorption)		Normalised DEHT area (%)
			d8-toluene (IS) (m/z 98)	DEHT (m/z 261)	
50	11.1	Tenax	5,230,139	16,249	0.3
	12.0	MS1	5,418.478	14,786	0.3
100	9.9	Tenax	4,808,349	15,133,147	315
	12.8	MS1	5,724,332	18,732,934	327
100	9.2	Tenax	3,746,625	37,440,141	999
	9.4	MS1	3,976,225	31,767,340	799
100	10.8	Tenax	3,820,066	32,978,961	863
	11.8	MS1	3,751,664	38,612,349	1,030

5.3.3 Determination of formaldehyde using TD

No formaldehyde was detected from the FLEC system with an empty desiccator using the acetylacetone (acac) method and an air sample volume of 30 litres. The concentration of formaldehyde determined using this method after addition of the plywood was 0.10 mg m^{-3}. On addition of a Tenax TA tube to the pathway, between the FLEC and the gas washing bottles, a further 30 litre air sample gave a similar concentration of formaldehyde (0.12 mg m^{-3}) showing that (as expected) formaldehyde was not trapped by the Tenax TA. TD/GC/MS analysis of the Tenax TA tube showed

the presence of hexanal. Other aldehydes, including hexanal, are often observed in the emissions of wood based products (see references in Table 1-5).

2-HMP eluted as a very broad peak on the DB-5 GC column (which had been chosen for standard VOC analyses). While not optimum for this work, the analytical conditions selected did allow separation of this compound from its derivative, formaldehyde oxazolidine (FO) (Figure 5-10). A calibration curve obtained is shown in Figure 5-11. The amount ratio represents the amount of formaldehyde used to form the derivative, divided by the amount of internal standard (diacetone alcohol) added (50 ng).

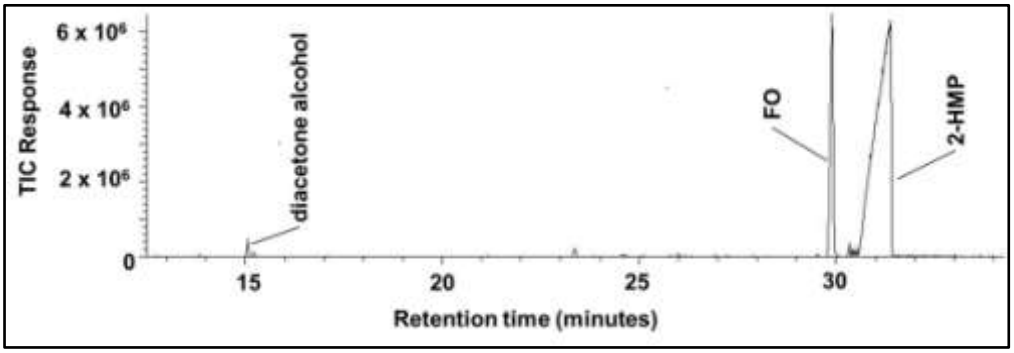

Figure 5-10 Chromatogram of 2-HMP and its formaldehyde derivative (FO) analysed on a 60 m DB-5 GC column

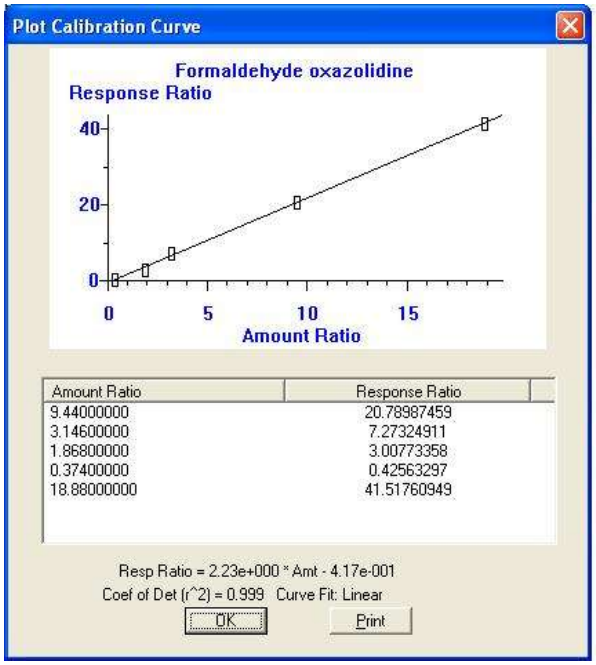

Figure 5-11 Calibration curve for formaldehyde obtained using 2-HMP method (each point represents the mean of two values)

With a filter placed at the front of a Tenax TA tube it was found to be still possible to achieve a flow of 200 ml min^{-1} through the system with the Casella TUFF air sampling pump. Analysis of the tube which had been used to sample 30 litres of air from the desiccator containing plywood with a clean filter, gave a similar chromatogram to that without the filter, while the acac method gave a value of 0.13 mg m^{-3}. A Tenax TA tube which had been fitted with a filter spiked with 1 µl 2-HMP solution and used to sample from the FLEC gave a significant peak due to the reaction product FO. A peak area of 51.8 million counts was recorded for the 97 ion (no internal standard had been added to allow quantification of this amount). The formaldehyde concentration recorded using the acac method, however, did not show a reduction, again giving a value of 0.13 mg m^{-3}. So it is clear that, while a small proportion of the formaldehyde present is reacting with the 2-HMP, the vast majority is still reaching the deionised water gas washing bottles. A number of experiments were therefore undertaken with the aim of improving the efficiency of this reaction and understanding the limitations of the method. The results of these are described in the following sections.

5.3.3.1 Increased volume of spiking solution

Amounts of FO obtained from analysis of three tubes fitted with filters each spiked with 5 µl of 2-HMP in methanol solution (2,600 ng $µl^{-1}$) and placed in line upstream of the gas washing bottles are shown in Figure 5-12. These were used to sample 2, 6 and 18 litres of air from the desiccator containing plywood.

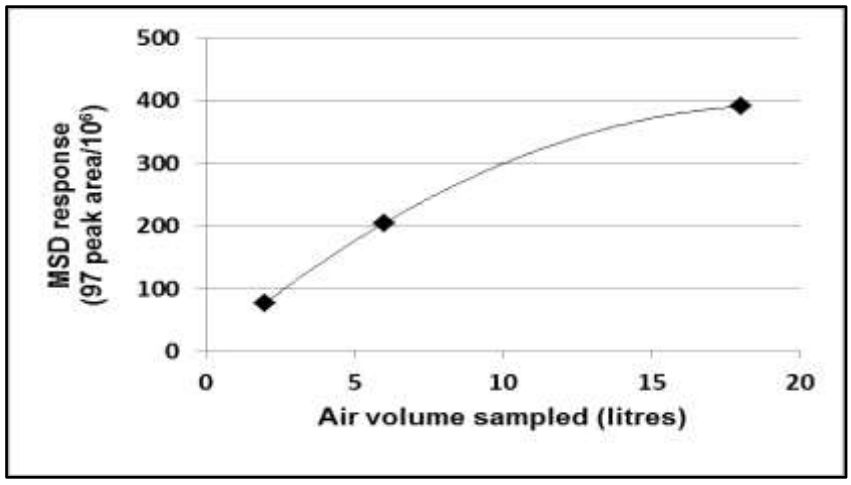

Figure 5-12 Amount of FO obtained using three different volumes of air to sample from a formaldehyde atmosphere

There is a suggestion of a decline in the amount of FO obtained per litre of sample volume with increasing amount of air sampled. This is consistent with the findings of the acac method which gave a formaldehyde concentration of 0.13 mg m^{-3} from the gas washing bottles placed in series behind the tube used to take the 18 litre air sample, compared with a value of 0.21 mg m^{-3} for this method without a sorbent tube or spiked filter in-line. Therefore the 2-HMP is reacting with a significant proportion of the formaldehyde in this case but, with this sample volume at least, a considerable amount is still reaching the water in the gas washing bottles.

A control sample taken using 5 µl 2-HMP solution spiked onto a filter fitted into the front of a conditioned Tenax TA tube and used to sample 18 litres air from the FLEC outlet with an empty desiccator gave a 97 ion peak area of 2.9 million. This represents 4 % of the area of the FO peak given by the 2 litre air sample from the plywood atmosphere (and 1 % of that from the corresponding 18 litre air sample). This shows that there is a small background of formaldehyde at some point in the process which requires further investigation.

5.3.3.2 Use of a 6.5 mm filter

Using one 6.5 mm PTFE filter impregnated with 40 µl of the solution of 2-HMP in methanol and fitted into a gauze cap, five conditioned Tenax TA tubes were used to take 2 litre air samples from the FLEC containing plywood, i.e. a total of 10 litres of air was passed through the filter, but the tube was changed after each 2 litre volume. The results obtained are shown in Figure 5-13. The FO peak area obtained is seen to decline first gradually and then more sharply as the reagent is depleted. This is confirmed by a parallel decline in the size of the peak due to the 2-HMP reagent in these chromatograms. This gives an idea of the capacity of the reagent, though this will depend on the efficiency of reaction which may be affected by other factors, including flow rate through the sampler (which was investigated in the following experiments). The use of the 6.5 mm filters, in conjunction with a gauze cap, was found to be more convenient than handling the smaller filters, so these were employed for further experiments. The use of 40 µl of the 2-HMP reagent was adopted for future experiments as, while it resulted in a very large broad peak in the chromatogram due to the excess

reagent, this was not found to cause a problem with the integration of the FO peak. An empty tube analysed on the analytical system after a tube containing a large 2-HMP peak was also found not to result in significant build-up of the compound in the analytical system.

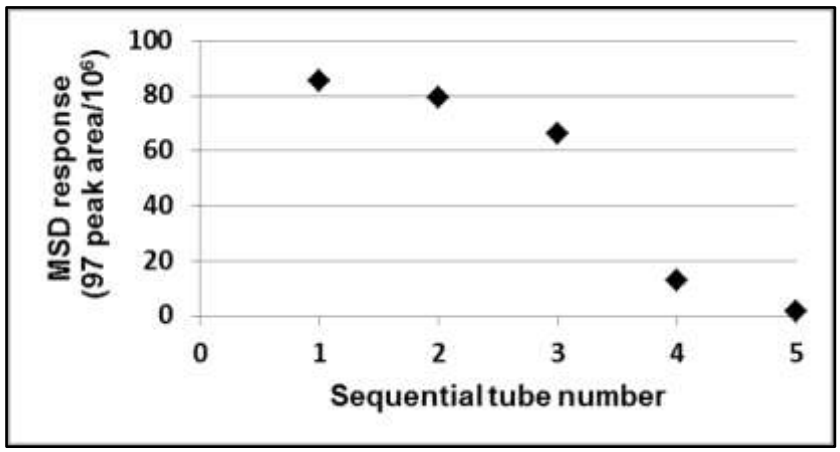

Figure 5-13 Amount of FO obtained from Tenax TA tubes used to take sequential air samples using the same spiked filter from a desiccator containing plywood

In the NIOSH method for formaldehyde using 2-HMP (NIOSH, 1994) the chemical is coated onto XAD-2 sorbent which air is then passed through during sampling. The flow rate is limited to 100 ml min^{-1} because of concerns about breakthrough owing to incomplete reaction. It was therefore decided to investigate whether a reduction in the flow through the samplers from 200 ml min^{-1} to 50 ml min^{-1} would give an improved level of trapping by the 2-HMP reagent.

5.3.3.3 Comparison of stainless steel and glass tubes

The first experiment undertaken using the lower flow rate was a repeatability test with six consecutive air samples taken alternating use of glass tubes packed with Tenax TA sorbent and standard stainless steel Tenax TA tubes. Sampling was undertaken from the FLEC for 30 minutes in each case to give sample volumes of 1.5 litres. Three samples were also taken from an empty desiccator using these conditions and one sample was taken from the desiccator containing the plywood using a filter with no reagent. Results obtained are shown in Table 5-8. No significant difference (t-test, 95 % confidence) was found in the mean formaldehyde concentrations recorded using the tubes made of the

two types of material. No advantage of the presence of glass is therefore being observed for this process. The level of formaldehyde recorded for control samples taken from an empty desiccator using these conditions was at a higher level (mean peak area of 7.0 million or 10 % of the sample peak area) than was found previously, this is probably due to the use of a greater volume of the 2-HMP reagent to spike the filters.

Table 5-8 Concentration of formaldehyde recorded in 1.5 litres air exiting a FLEC with and without plywood using the 2-HMP method and two types of Tenax tubes

	Formaldehyde concentration (mg m^{-3})			
	With plywood			**Control – empty desiccator**
Tube type	**Stainless steel – no 2-HMP**	**Stainless steel**	**Glass**	**Stainless steel**
Mean	Not detected	0.23	0.21	0.02
RSD	---	10.5 %	8.9 %	28 %
n	1	3	3	3

5.3.3.4 Comparison of the 2-HMP and acac methods using the lower flow rate

Three sample volumes were tested with, in each case, a pair of air samples taken first with a filter coated with 2-HMP reagent in front of a Tenax TA tube and second using an uncoated filter. Amounts of formaldehyde breaking through the Tenax tube were determined by use of the acac method downstream. Note that these three tests were carried out on different days so there could be some difference in the formaldehyde concentration for the different air sample volumes. The results obtained are shown in Table 5-9. For a 40 minute air sample (2 litres air), the amount of formaldehyde found on the tube using the 2-HMP method was 615 ng which represents a concentration in the air of 0.29 mg m^{-3}. No formaldehyde was found using the acac method. For this air volume without any 2-HMP present, the acac method gave a formaldehyde concentration of 0.18 mg m^{-3} and the 2-HMP method showed no FO peak. Similar results were obtained for sample volumes of 3 and 6 litres. It is of interest to note that hexanal was observed in each of the chromatograms obtained from sampling without the 2-HMP reagent, but not in those where the reagent was present. This reagent is known to also react with other aldehydes, though a previous study reported that it could

not be used for their determination due to interference of the excess reagent peak (Veasey, 2000).

Table 5-9 Concentration of formaldehyde recorded by periodic sampling of the air exiting a FLEC containing plywood using acac and 2-HMP methods

Formaldehyde concentration (mg m^{-3})						
Sample volume (litres)	**2**		**3**		**6**	
With or without 2-HMP	**With 2-HMP**	**Without 2-HMP**	**With 2-HMP**	**Without 2-HMP**	**With 2-HMP**	**Without 2-HMP**
acac method	ND [2]	0.18	ND	0.16	ND	0.20
2-HMP method [1]	0.29	ND	0.26	ND	0.36 [3]	ND

[1] not blank subtracted; [2] ND = not detected; [3] approximate value, above top of calibration curve

These findings suggest that, with these sampling conditions, all the formaldehyde is being trapped by and reacting with the 2-HMP reagent. Higher concentrations were apparently detected using the 2-HMP method than the acac method, though caution needs to be exercised in interpreting these results as no control values have been subtracted from the formaldehyde concentrations obtained using the 2-HMP method. It is clear that some level of FO background is present, but further work is required to determine an appropriate control value to apply. Also the acac method, at these sample volumes, is being operated at the low end of its calibration range (e.g. for a 2 litre air sample the estimated lower limit of detection for this method is 0.12 mg m^{-3}) so there will be greater uncertainty in the concentrations determined. The comparison between the two methods would be improved by increasing the mass of formaldehyde being sampled (either using a higher concentration or a longer sampling time) which would be at a more optimum level for the acac method. For the 2-HMP method, the 6 litre sample gave a peak area above the top of the calibration range; in this case the use of higher split flows at the thermal desorber would allow quantification of greater amounts.

5.3.3.5 Test of multiple filters

For the 3 litre air sample described in 5.3.3.4 above, an extra test was undertaken in which three filters, rather than the normal one were placed in the gauze at the front of the tube. Each filter was spiked with 40 µl of the 2-HMP reagent. The concentration of

formaldehyde determined using the 2-HMP method was in this case 0.24 mg m^{-3}, i.e. comparable to that obtained using a single filter. Therefore, for this sample volume and formaldehyde concentration, no advantage is being gained from use of a greater amount of reagent or greater depth of reagent bed. However, as it was possible to maintain the required sampling rate, this test shows the potential for higher loadings to be determined i.e. higher concentrations and /or longer averaging periods.

5.3.3.6 Test of blank level of 2-HMP solution

The blank level of the 2-HMP solution was examined by injecting 5 µl of the 2-HMP reagent into each of five conditioned Tenax TA tubes. This was repeated with a further three tubes and 40 µl of the solution. The 5 µl injections gave a mean formaldehyde concentration of 27.0 ng on the tube (RSD 12.6 %), while the 40 µl injections gave a mean of 53.5 ng on the tube (RSD 3.5 %). The 40 µl injection result represents 15 % of the mass on the tube for a 1.5 litre air sample at a concentration of 0.22 mg m^{-3} (as in Table 5-8) and 3 % of that for a 6 litre sample at a concentration of 0.36 mg m^{-3} (as in Table 5-9). This is the potential background level were the entire reagent from the filter to be volatilised and pass onto the sorbent during sampling. This does not, however, take into account the additional background that could arise from formation of the derivative which might occur during the spiking of the reagent onto the filter, the drying of the solvent, transfer of the filter to the gauze and any storage time before air sampling.

5.3.3.7 Analysis of filters after use for sampling

There also exists the possibility that some FO remains on the filter following air sampling rather than all of it passing onto the sorbent. To test for this two used filters from the repeatability test undertaken in Section 5.3.3.3 were removed from the gauzes and placed in glass vials then 100 µl of methanol was added to each. The filter used to sample from the plywood atmosphere without the addition of 2-HMP and a filter which had been spiked with the reagent, but not used for sampling, were treated in the same way. The vials were left to stand for 30 minutes after which time 10 µl of solution from each were spiked into conditioned Tenax TA tubes and the tubes were analysed (after purging off the methanol). The results obtained (Table 5-10) suggest that a measurable amount of formaldehyde (in the form of FO) is retained on the filters following air

sampling. However, as both the filter which had been used but not spiked with reagent and that which had been spiked but not sampled also showed the presence of formaldehyde, it is possible that some contamination exists, perhaps in the syringe. Formaldehyde in the atmosphere may also be reacting with the reagent in solution. Further investigation of this background level using a greater number of filters is required.

Table 5-10 Amount of formaldehyde found from filters used for spiking with 2-HMP reagent

Filter treatment	Unspiked but sampled	Spiked and sampled 1.5 litres air from formaldehyde atmosphere		Spiked but not sampled
Amount of formaldehyde (ng on tube)	22.3	44.8	33.8	46.2

5.3.3.8 Comparison with previous work

The findings of the present study have confirmed those of the previous work by Veasey (2000) which suggested that 2-HMP reagent is suitable for the determination of formaldehyde using a thermal desorption process. The previous study made use of an Optics Programmable Temperature vaporiser which was a manually operated unit with the desorption flow being controlled by use of the split flow. This resulted in compromises having to be made between sufficient desorption flow in order to sweep the analyte off the tube and minimal split flow to give sufficient sensitivity. The present work, in contrast, has made use of an automated two-stage thermal desorption system in which desorption and split flows are independent of each other. In the present work a split flow of 10 ml min^{-1} was employed giving a split ratio of 9:1. An increase of this setting to enable better comparison with the acac method should therefore not affect the desorption process. The system applied in the present work also benefits from use of sampling tubes having a significantly greater mass of sorbent (approximately 200 mg) compared with the work by Veasey (2000) which used a sorbent mass of 40 mg. This results in greater sample capacity before breakthrough occurs. While the previous study used glass sorbent tubes, the present work has shown that stainless steel, which has the advantage of being less fragile, is also a suitable material to use.

The study by Veasey (2000) trialled the use of filters which were coated in a solution of the reagent and inserted into the front of the tube, achieving a relative standard deviation for repeat analyses of 15 %. The present work obtained a repeatability of 10 % using a development of this technique in which the filters were inserted into separate gauzes. While easier, this technique would still be difficult to undertake as a routine operation. The whole process of preparation of spiked filters, their insertion into the gauzes and storage prior to sampling is also likely to be contributing to the blank level of the method. If this technique was to be employed routinely, it would ideally be undertaken in a low formaldehyde atmosphere, with the prepared gauze sealed in protective pouches as is the case for cartridges coated with 2,4-dinitrophenylhydrazine for the determination of formaldehyde using HPLC (Waters, 2009). Veasey (2000) switched from use of toluene to dichloromethane as the solvent for delivering the 2-HMP reagent onto the filters to minimise retention of solvent on the Tenax. In the present study methanol, which is the solvent of choice for preparation of solutions of VOCs for analysis using thermal desorption (see Section A.5.10), has been used as the solvent. Methanol has the advantage of being retained to an even lower extent than is dichloromethane on Tenax. No problems were identified with use of this solvent, though a comparison of the performance of methanol and dichloromethane as solvents for spiking onto filters would be useful.

As identified in Section 1.5.2, two other reagents for preparation of thermal desorption amenable derivatives of formaldehyde have been studied by other workers, namely pentafluorophenyl hydrazine (PFPH) and (pentafluorobenzyl)-hydroxylamine hydro-chloride (PFBHA). These would have an advantage over 2-HMP of being suitable for the determination of a wider range of carbonyl compounds (Ho and Yu, 2004). These authors found sample flow rates of > 20 ml min^{-1} to result in deterioration in the collection efficiency for carbonyls using PFBHA, whereas a flow rate of 100 ml min^{-1} could be applied using PFPH. In this previous work PFPH was applied onto the sorbent itself, so the possibility of employing it in the form of spiked filters would be worthy of exploration. PFPH has an additional advantage of being 10 times cheaper than PFBHA, an important factor in the selection of a reagent for routine use for emissions testing (in comparison with 2-HMP, PFPH is approximately half the cost). In the present study breakthrough of formaldehyde was observed for the higher flow

rates/sample volumes used. Further studies comparing the performance of 2-HMP and PFPH reagents at a range of flow rates/sample volumes would therefore be beneficial.

5.4 Conclusions

The work undertaken in support of this objective has made significant progress in the determination of VVOCs in material emissions. A multi-sorbent tube containing quartz wool/Tenax TA/Carbograph 5TD has been found to result in a marked extension of the volatility range of compounds which can be determined from one sampler, compared to use of Tenax TA alone. While not a complete test of breakthrough performance, the findings of the project suggest that this multi-sorbent tube can be used to determine, up to a sample volume of at least 10 litres, six VVOCs which appear on at least one target list of chemicals of concern in material emissions. In comparison, the maximum safe sample volumes for these compounds using Tenax TA alone ranged from <200 ml to 3.5 litres. More modest improvements in the maximum safe sampling volume possible were identified for 11 other VVOCs emitted from materials, and/or also occurring on one or more target list. Further tests in a humid atmosphere and with greater control of temperature and analyte loading levels are recommended, however, to confirm breakthrough volumes. Other sorbent combinations, including a carbon molecular sieve, could also be tested, whilst taking into account the greater effect of moisture and more complex calibration procedure involved with using such sorbents.

The use of Nalophan bags was found to be a convenient means of generation of an atmosphere of different mixtures of VVOCs for comparing the performance of different sorbent types for several compounds simultaneously. Together with screening tests of material emissions these were successfully used to compare the performance of sorbents for VVOCs and VOCs. The studies conducted have, however, highlighted the difficulty in working with SVOCs, including the long sampling times required and a challenge for the analytical equipment. The use of the μ-CTE at an elevated temperature was found to allow a speedier comparison of the performance of sorbents with an SVOC than using an ambient temperature. From the tests undertaken, no improvement in performance was identified for the compound selected for study, DEHT, which has a boiling point of 400 °C. Further work could test several samples at the same time in the μ-CTE and also

look at performance for other compounds. It might be of interest to assess recovery of some aliphatic hydrocarbons of chain length from that of n-docosane (C_{22}) upwards to investigate the limits of the method further.

The investigations undertaken using 2-hydroxymethylpiperidine (2-HMP) have confirmed its potential to act as a derivatising agent for the quantitative determination of formaldehyde in air by thermal desorption. The introduction of the reagent onto a filter placed inside a gauze cap fitted to the front of the tube was found to be an improvement over previous application methods. The use of the 2-HMP and acetylacetone methods in series have demonstrated the efficiency of 2-HMP in removing formaldehyde from the air flow. This has shown that use of a sintered PTFE filter with a loading of 40 µl of a 2,600 ng μl^{-1} solution of 2-HMP reagent, and sampling volume of 1.5 – 3 litres was appropriate for determination of a formaldehyde concentration in the range 0.1 – 0.3 mg m^{-3}. More data on background levels are required and further work with the sensitivities of the two methods more aligned could explain the apparent greater concentrations of formaldehyde being recorded using the 2-HMP method.

The VVOCs/sorbents aspects of this work have been published in the journal Analytical Methods and details can be found in Appendix G.

6 INVESTIGATION INTO THE PERFORMANCE OF A TOF MS FOR THE DETERMINATION OF TARGET COMPOUNDS IN MATERIAL EMISSIONS

6.1 Introduction

The fourth objective of the project was to develop a method for the determination of compounds of interest in material emissions using an analytical system incorporating a time-of-flight (TOF) mass spectrometer (MS). The performance of the method could then be compared to that for the system incorporating standard MS technology. The main potential benefit of the use of a TOF MS is its expected greater sensitivity, which is a particular issue for detection of carcinogens in particular. It also scans at a faster rate than conventional MS which could allow the future development of methods based on fast GC. The principles of TOF technology were introduced in Section 1.5.4 and details of the hardware and software making up the system used are given in Section 2.4. As this was both a newly installed instrument and new technology, the initial focus was on commissioning the system and optimisation of parameters. This work is described in the following section and a procedure developed for the application of this instrument to material emissions testing is included as Appendix A.6. Further sections of this chapter describe the calibration of the system for two sets of target compounds and its application to the determination of these compounds in chromatograms from an emissions test.

6.2 Methods

6.2.1 Instrument set up and optimisation of parameters

6.2.1.1 TD settings

For maximum sensitivity, analysis of material emissions samples using the analytical system incorporating a TD-100 and an MSD was normally undertaken using no inlet split flow and the minimum outlet split flow recommended (given the requirement to desorb high boiling compounds). With the expected greater sensitivity of the TOF MS, adjustment of split flows was expected to be necessary depending on the concentration

of the target compounds. Setting of split flows on this instrument was undertaken by adjustment of the appropriate needle valve on the TD and recording the flow using a flow meter. In order to quantify compounds emitted from the material in widely different amounts, two air samples from an emissions test could be analysed using different split ratios. Alternatively, an option exists to undertake two analyses from one air sample by making use of the re-collection facility available on the TD. First a high split ratio would be used to quantify those compounds occurring in a high amount, followed by analysis of the split effluent using a low split to detect those compounds present in trace amounts and which are required to be determined to a low level. Optimisation of the system for analysis of material emissions therefore required the development of two methods with differing sensitivity with adjustment of split flows in between.

6.2.1.2 GC parameters

As used in the MSD system, the instrument was fitted with a 60 m DB-5 column of internal diameter (I.D.) 0.25 mm and film thickness 0.5 µm. The temperature programme applied was also the same as for the MSD system. The TOF MS was set up with a 2.5 m length of 0.15 mm I.D. fused silica tubing inserted into the transfer line and ion source (to allow maintenance, such as changing the column, to be undertaken without venting the instrument). This is equivalent to adding an extra 18 m length of a 0.25 mm diameter column to the system and therefore required a higher pressure to maintain the same flow. Initially a flow rate of 1.2 ml min^{-1} was set, later the pressure regulator (Gas01) was by-passed to allow the flow rate to be increased to 1.3 ml min^{-1} to allow a shorter run time and closer comparison with the MSD system.

6.2.1.3 TOF scan range

The TOF has a maximum scan range of m/z 1 to 1000. Initially the same scan range as used in the MSD system (m/z 20-450) was applied, but this was later changed to m/z 35-450 on advice from Markes (to minimise damage to the micro-channel plates in the event of an air/water leak).

6.2.1.4 TOF filament voltage

The value at which the filament voltage is set determines the emission current. Larger emission currents result in improved sensitivity, but will increase the noise as well as the signal and can reduce the lifetime of the filament. On installation of the instrument the filament voltage was set at 1.70 V. Tests were undertaken to investigate performance for values between 1.5 and 2.0 V.

6.2.1.5 TOF data (Scanset) rate

The TOF scans at a significantly faster rate than a conventional quadrupole MS. It acquires 10,000 full mass range spectra a second and packages these together into 'scansets' to minimize data storage requirements. The scanset (or data) rate is the number of data points. For conventional chromatography values of around 2-3 points per second are recommended, though the TOF can sample at a rate of 40 Hz, or even greater for high speed analysis. The data rate required is set by selecting the number of scans per scanset value in the software. In order to select a suitable value, replicate analyses of the 11 compound check standard mixture (see Section 1.4.1) were undertaken using scans/scanset settings of between 2,500 and 7,500. These are equivalent to data rates of between 1.3 and 4.0 Hz.

6.2.1.6 TOF ion source and transfer line temperatures

The default settings for the ion source and GC-TOF transfer line temperatures were both 200 °C, with a maximum temperature of 300 °C. Initially the default values were used, with both later being increased to 230 °C to give improved peak shape for higher boiling compounds.

6.2.1.7 Repeatability of instrument

Repeatability of analysis of replicate tubes was investigated by spiking three sets of conditioned Tenax TA tubes each with the same amount of the check standard solution followed by analysis using an appropriate split ratio for each set of tubes.

6.2.2 Calibration of system

Initially three multi-level calibrations of the system were undertaken for the check standard solution with analysis at different TD split ratios. Two replicate Tenax TA

tubes were used for each loading level and 0.5 µl of a solution of d8-toluene in methanol was added to each tube to act as an internal standard (see Section 2.5.2). To give the low sensitivity setting, a further calibration for these compounds was undertaken using a split ratio of ~450:1. For the high sensitivity setting, calibrations were undertaken using a split ratio of ~9:1 for the check standard mixture and for a mixture of 11 compounds classified as carcinogens on one or more target lists of compounds identified from the literature review (see Section 2.5.1). These compounds are listed in Table 6-1. Tubes packed with the multi-sorbent, MS1 (see Section 2.3.1) were used for the high/low sensitivity work. A study of blank levels was also undertaken at the high sensitivity setting involving repeat analysis of empty tubes, conditioned tubes and tubes just spiked with the internal standard.

Table 6-1 Details of compounds studied using the TOF system which are identified as carcinogens on one or more target lists

Compound	CAS Number	Boiling point (°C)	Retention time on TOF system (minutes)	Target lists found on ¶
Acrylonitrile	107-13-1	77	7.4	b,c,g,h,j,k,n
1,2-Dichloroethane	107-06-2	84	11.7	a,c,g,h,j,k,n,o
Benzene	71-43-2	80	12.4	a,b,c,f,g,h,i,j,k,l,m,n,o
Trichloroethylene	79-01-6	87	14.4	a,c,f,g,h,i,j,k,n,o
1,3-Dichloropropan-2-ol	96-23-1	174	27.4	c,g,h,o
Benzyl chloride	100-44-7	179	33.5	c,g,h,j,k,n
o-Toluidine [o-methylaniline]	95-53-4	200	35.7	c,g,h,j,k,n
o-Anisidine [2-methoxyphenylamine]	90-04-0	225	38.8	c,g,h,j,k,n
4-Chloroaniline	106-47-8	232	39.5	c,g,h,k
Dibutyl phthalate	84-74-2	340	50.0	a,f,j,k
Di-2-ethylhexyl phthalate (DEHP)	117-81-7	384	56.9	f,j,k

¶ see Table 2-1 for key to lists of chemicals

In order to check the high/low sensitivity method, tubes containing a high level of the check standard mix and a lower level of the carcinogen mix were analysed using the high split method with the split effluent being re-collected onto a conditioned tube. The re-collected tubes were then analysed using the low split method. A level of carcinogen mix was selected which would be at the detection limit of the low sensitivity method. Four conditioned MS1 tubes were tested as follows: 1) internal standard (IS) only, 2) IS plus 1 µl of the ~3 ng μl^{-1} carcinogen mix, 3) IS plus 1 µl of the ~ 250 ng μl^{-1} check standard mix, 4) IS plus both the carcinogen mix and the check standard mixture. The re-collected tubes were analysed together with a tube freshly spiked with IS and one freshly spiked with IS plus 1 µl of the ~3 ng μl^{-1} carcinogen mix.

6.2.3 Application to material emissions testing

In order to demonstrate the detection of low levels of carcinogens within a complex matrix produced by material emissions, a standard mixture of the carcinogens was spiked onto tubes used to test the emissions from a vinyl floor tile. To achieve this, the material was exposed in the FLEC and duplicate samples of approximately 5 litres of the exit air was taken using conditioned MS1 tubes after 3 and 21 days. One of each pair of sampled tubes was spiked with 1 µl of the ~3 ng μl^{-1} carcinogen mix and all four tubes were analysed with the high split method with re-collection onto conditioned tubes. The re-collected tubes, together with two fresh tubes spiked with the internal standard only and two spiked with the internal standard and the carcinogen mix, were analysed using the low split method.

6.3 Results and Discussion

6.3.1 Instrument set up and optimisation of parameters

6.3.1.1 TOF filament voltage

A first comparison of filament voltages involved two sets of seven replicate tubes, each spiked with approximately 100 ng of each of the check standard compounds, one of which was analysed on the TOF system using a filament voltage of 1.7 V and the other using a value of 2.0 V. Auto Signal Optimisation' (ASO, instrument tuning) was undertaken after adjustment of the voltage as recommended in the instrument

documentation. A split ratio of approximately 40:1 was used for this test. The mean responses found for each compound at each setting, together with signal to noise values from one random chromatogram recorded at each setting, are given in Table 6-2. The table also shows RMS (root mean square) signal to noise (S/N) values obtained using extracted ions from one of the chromatograms, selected at random, for each filament voltage. For this the S/N tool within ChemStation was used which involved selection of a number of scans across the peak, followed by selection of an area of the background to give the noise value. With the exception of butylated hydroxytoluene (BHT), the responses at 2.0 V for all compounds were significantly higher than at 1.7 V (t-tests, 95% confidence), which might suggest that the instrument is more sensitive at the higher voltage setting. However, the signal to noise values were lower for most compounds at the higher voltage. The use of a filament voltage of 2.0 V would not therefore seem to be offering a consistent advantage over 1.7 V. The use of the higher filament voltage would also be likely to result in a shorter filament lifetime. The cost of replacement filaments is a consideration, as is the downtime incurred to fit them as this would involve venting the instrument.

Table 6-2 First investigation of optimum filament voltage for TOF system

Filament voltage	**1.7 V**		**2.0 V**	
Compound	**Mean Response (n=7)**	**S/N (n=1)**	**Mean Response (n=7)**	**S/N (n=1)**
D8-toluene	30,182,541	115,389	54,191,154	62,150
n-Hexane	19,239,238	19,764	35,320,682	6,740
MIBK	51,531,150	44,383	70,476,911	24,781
Toluene	58,928,001	124,806	75,914,490	58,472
Hexanal	22,616,144	13,267	46,589,870	14,684
Butyl acetate	56,921,653	35,852	69,712,162	17,734
Cyclohexanone	39,428,357	37,981	48,796,207	20,909
Phenol	26,001,793	55,153	38,848,628	61,590
123-TMB	41,623,460	212,530	45,795,133	126,044
4-PCH	35,188,854	112,169	37,390,395	80,692
BHT	28,654,402	42,975	28,309,325	45,502
n-Hexadecane	19,492,637	2,327	28,386,523	1,083

A second comparison of filament voltages involved sets of replicate tubes loaded with 100 ng of the check standard compounds and analysed using filament voltages of between 1.5 and 1.8 V. (Different numbers of replicates were achieved in each case due to instrument problems). The mean responses found for each compound at each setting are given in Table 6-3 (note that these responses cannot be compared with those above as the two experiments used different data rates). While the responses increase with increasing filament voltage and the tendency is the same with the signal to noise ratios, the latter are not so consistent. Nevertheless the conclusion can be drawn that 1.5 V would result in too low a level of response, while 1.6-1.8 V give high levels of response and signal to noise ratio. 1.7 V was therefore selected for further work.

Table 6-3 Second investigation of optimum filament voltage for TOF system

Filament voltage	**1.5 V**	**1.6 V**	**1.8 V**	**1.5 V**	**1.6 V**	**1.8 V**
Compound	**Mean Response**			**S/N (n=1)**		
	n=4	**n=5**	**n=2**			
D8-toluene	432,437	5,021,501	18,659,622	4,618	83,060	63,300
n-Hexane	316,771	5,405,747	18,266,841	1,105	3,478	18,962
MIBK	874,509	11,237,041	26,708,328	2,131	3,195	8,668
Toluene	1,536,228	17,126,410	38,434,499	2,699	35,801	126,474
Hexanal	335,071	5,238,516	13,150,555	154	941	2,939
Butyl acetate	1,151,264	13,569,467	26,500,267	889	4,035	11,729
Cyclohexanone	543,627	6,744,462	12,776,443	4,871	27,810	13,584
Phenol	685,011	5,159,512	11,984,793	7,195	26,951	20,334
123-TMB	1,414,751	11,289,988	18,614,830	5,536	9,711	86,409
4-PCH	2,684,759	14,835,718	19,477,984	26,070	50,104	66,290
BHT	1,395,903	6,146,012	9,006,033	61,861	6,999	144,437
n-Hexadecane	331,038	2,725,975	7,996,988	1,342	2,231	949

6.3.1.2 TOF data rate

Four sets of five replicate tubes, each spiked with approximately 2.5 ng of each of the 11 check standard compounds, were analysed on the TOF system using a range of scans/scanset values in order to investigate the optimum data rate for this analysis. The ASO process was undertaken after each adjustment of the scans/scanset setting. The TD

was set up with no inlet split and a minimum outlet split to give a split ratio of approximately 9:1 for this test. The mean responses found for each compound at each setting, together with signal to noise values obtained using extracted ions from one of the chromatograms for each data rate, are given in in Table 6-4.

There is a suggestion of a decreasing response with increasing data rate (which might result in a reduction in instrument sensitivity), but no comparable reduction in signal to noise is observed. The S/N values can also be used as a first comparison of the sensitivity of the TOF system with that of the MSD system. The S/N values obtained from analysis of the same loading level of the check standard solution (i.e. 2.5 ng on the tube) using the full scan setting on the MSD system, as part of the study of the limits of quantitation of the system (See Table C-17 in Appendix C) were all lower than 1,000, except for 4-PCH, for which a value of 1,022 was obtained. In comparison, values of 10,000-15,000 were obtained for 4-PCH on the TOF system, with most of the other compounds also showing values significantly greater than 1,000. This is a suggestion that substantially higher sensitivity is being achieved using the TOF system.

The packaging of data from each scan into a scanset within the TOF software means that the accuracy of the quantitation should be maintained at low data rates, but this needs to be balanced against the greater accuracy with which retention times can be recorded with a larger number of data points across a peak, which is of advantage when using TargetView for data processing. Also to be taken into account is the size of the files generated for each analysis. Several different files are saved per run, the largest of which is the ProtoTOF '.dat' file. The size of this was found to increase from 385 MB for an analysis using a data rate of 1.3 Hz, to 1,149 MB for an analysis using a data rate of 4 Hz. Use of a data rate of 2.2 Hz gave a file size of 641 MB. A data rate of 2.2 Hz was felt to give a good compromise between retention time accuracy and data file size and was therefore applied for further analysis using this instrument.

Table 6-4 Investigation of optimum data rate for TOF system

Scans/scanset	**7,500**	**4,500**	**3,500**	**2,500**	**7,500**	**4,500**	**3,500**	**2,500**
Data rate (Hz)	**1.3**	**2.2**	**2.8**	**4.0**	**1.3**	**2.2**	**2.8**	**4.0**
Compound	**Mean Response (n=5)**				**S/N (n=1)**			
D8-toluene (50 ng on tube)	67,581,596	57,469,906	47,919,341	32,064,491	52,625	42,789	97,994	101,446
n-Hexane	3,351,724	2,026,459	1,405,773	640,273	1,687	1,820	1,774	1,466
Methyl isobutyl ketone (MIBK)	7,833,090	3,856,127	3,254,436	1,424,715	2,059	1,315	2,021	12,232
Toluene	12,536,186	7,139,085	5,186,589	2,783,613	32,162	25,402	19,212	21,560
Hexanal	5,985,230	3,175,849	2,623,304	1,249,045	871	485	818	919
Butyl acetate	9,099,804	4,589,930	3,791,693	1,595,899	1,961	1,244	2,072	1,095
Cyclohexanone	4,166,635	1,935,933	1,706,501	736,475	839	1,040	1,938	506
Phenol	15,955,393	6,026,650	4,127,543	1,742,484	18,280	8,184	12,783	8,486
1,2,3-Trimethylbenzene (123-TMB)	10,934,762	5,509,927	4,557,626	2,120,919	60,406	64,508	40,553	71,005
4-Phenylcyclohexene (4-PCH)	15,725,217	7,222,144	6,366,786	2,890,020	14,232	13,577	14,818	10,513
Butylated hydroxytoluene (BHT)	8,027,553	3,237,981	2,863,150	1,413,643	57,973	43,609	35,044	76,496
n-Hexadecane	3,572,995	1,393,480	1,398,335	563,014	2,672	2,529	3,255	2,914

6.3.1.3 Repeatability of instrument

The results obtained on analysis of three sets of replicate tubes spiked with either the 2.5 or 100 ng level of the check standard compounds using a range of instrument settings is given in Table 6-5. With a few exceptions, good repeatability was obtained for all compounds. Phenol gave a very high variability for one set of repeat injections, with values above 10 % also been observed for hexanal and n-hexadecane for that set of results. Phenol and hexanal, due to their polarity, are expected to be the first compounds to give poorer results (see Section 1.4.1) as a result of contamination in the system. This was investigated and some dark spots were observed in the tubing fitted between the GC column and the TOF ion source. The system was vented to allow replacement of this tubing and its connection fitting which resulted in improved peak shapes and repeatability, as shown in the data in the right hand columns of Table 6-5.

Table 6-5 Repeatability of standard mix analysed on TOF system using different instrument settings

Compound	100 ng mix with split ratio ~ 40:1 and filament set at 1.7 V		2.5 ng mix with split ratio ~ 9:1 and filament set at 1.7 V		100 ng mix with split ratio ~ 40:1 and filament set at 1.6 V	
	Response (n=7)		Response (n=5)		Response (n=7)	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
D8-toluene	13,250,725	3.8	65,084,268	1.6	3,765,153	1.9
MIBK	18,286,820	3.1	5,223,382	4.0	4,878,068	1.5
Toluene	24,257,100	1.7	9,646,350	6.8	8,424,947	1.8
Hexanal	10,293,965	5.2	5,495,557	13.5	1,876,020	1.6
Butyl acetate	19,663,950	1.9	6,089,406	3.7	6,379,598	1.1
Cyclohexanone	14,598,565	1.8	2,797,428	5.7	2,654,885	6.4
Phenol	13,563,124	2.6	9,338,342	47.0	3,714,766	2.8
123-TMB	26,739,067	2.0	7,934,565	4.3	6,157,028	1.7
4-PCH	25,530,467	2.0	11,738,902	3.0	9,602,919	2.5
BHT	17,200,548	2.8	6,149,955	10.1	5,742,492	2.6
n-Hexadecane	11,295,741	4.2	2,096,607	13.5	1,189,117	3.5

6.3.2 Calibration of system

6.3.2.1 Initial calibrations

The TD split ratios, approximate ranges of loading levels and linear ranges determined for the check standard compounds from the initial calibrations are shown in Table 6-6 (note that the amounts of different compounds in one loading level varies slightly).

Table 6-6 Linear ranges for check standard compounds on TOF using three different split ratios

Approximate split ratio	**10:1**	**40:1**	**250:1**
Approximate loading level range (ng)	**1-300**	**1-300**	**2.5-3,000**
Compound	**Linear range**		
n-Hexane	1-20	1-60	2.5-575
MIBK	1-24	1-82	2.5-820
Toluene	1-26	1-87	2.5-875
Hexanal	1-25	1-250	2.5-835
Butyl acetate	1-28	1-92	2.5-925
Cyclohexanone	1-29	1-300	3-990
Phenol	1-22	2-224	2.5-900
123-TMB	1-25	1-85	2.5-250
4-PCH	1-10	1-30	3-281
BHT	1-27	1-84	2.5-840
n-Hexadecane	1-24	1-80	2.5-800

For each of these cases, with the exception of hexanal, cyclohexanone and phenol at the split ratio setting of 40:1, the curves for each compound became non-linear below the highest loading level used, which means that the maximum quantifiable amounts for these settings (using a linear calibration) has been defined. It was not possible to determine the minimum detectable amounts at any of these settings, as the lowest loading level used was detected in all cases. The next calibration therefore included analysis of lower concentration standard solutions.

6.3.2.2 Set-up of high/low sensitivity settings

A split ratio of ~450:1 was found to be appropriate for the low sensitivity setting, giving approximately the same linear range for the check standard compounds as was achieved using the MSD system in full scan mode with the minimum split ratio i.e. typically 3-1,000 ng on the tube. Results obtained are shown in Table 6-7 (note that this mixture did not contain n-hexane but did include m-xylene, α-pinene and limonene not present in the previous check standard mixture). A split ratio of 9:1 resulted in the curves for the check standard compounds becoming non-linear above a tube loading of around 20-30 ng. At the low end of the calibration most of the compounds were detectable from 0.1 or 0.3 ng. Good correlation coefficients (≥0.994) were observed for all these compounds at both sensitivity settings.

The mixture of carcinogens, analysed at the high sensitivity setting, showed similar linear ranges to those of the check standard mixture, i.e. ~0.1-30 ng on the tube. An exception to this was dibutyl phthalate which became non-linear at a level of 13 ng. Correlation coefficients were again good for most compounds, being ≥0.992 for all compounds except o-anisidine and 4-chloroaniline, for which values of 0.98 were obtained. A chromatogram of the carcinogen mixture is shown in Figure 6-1.

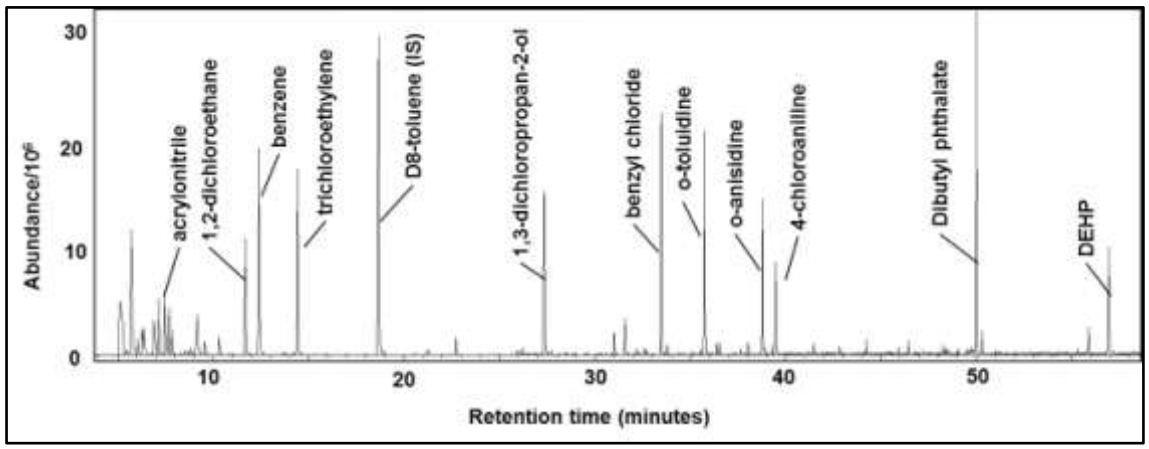

Figure 6-1 Chromatogram of mixture of eleven carcinogens, approximately 30 ng of each spiked onto tube and analysed on TOF MS system

Table 6-7 Linear ranges recorded using high and low split ratios

Approximate split ratio	**~450:1**		**~9:1**	
Approximate loading level range (ng on tube)	**0.3-900**		**0.1-90**	
Compound	**Linear range**	**Correlation coefficient**	**Linear range**	**Correlation coefficient**
Check standard compounds				
MIBK	8-800	0.996	0.3-30	0.995
Toluene	3-900	0.998	0.3-30	0.998
Hexanal	8-800	0.998	0.3-30	0.997
Butyl acetate	9-900	0.996	0.3-30	0.995
m-Xylene	1-800	0.997	0.3-30	0.998
Cyclohexanone	9-900	0.994	0.3-30	0.999
α-Pinene	0.3-900	0.998	0.1-30	0.995
Phenol	3-1,300	0.994	0.1-30	0.977
123-TMB	1-900	0.997	0.2-20	0.998
Limonene	2.5-850	0.996	0.1-30	0.996
4-PCH	1-1,000	0.998	0.3-30	0.990
BHT	1-1,000	0.998	0.3-30	0.999
n-Hexadecane	3-950	0.998	0.1-30	0.999
Carcinogen mix				
Acrylonitrile	Not tested		0.1-30	0.9998
1,2-Dichloroethane (12-DCE)			0.1-30	0.9998
Benzene			0.1-30	0.9994
Trichloroethylene			0.1-30	0.9999
1,3-Dichloro-propan-2-ol (13-DCP)			0.1-30	0.9980
Benzyl chloride			0.1-30	0.9991
o-Toluidine			0.1-30	0.9938
o-Anisidine			0.1-30	0.9856
4-Chloroaniline			0.1-30	0.9797
Dibutyl phthalate (DBP)			0.1-13	0.9996
Di-2-ethylhexyl phthalate (DEHP)			0.1-30	0.9917

6.3.2.3 Sensitivity study of TOF system

The sensitivity of the system was investigated using three repeat analyses of the ~0.3 ng loading level of the carcinogen mix (i.e. the second from lowest calibration level). Mean peak areas and S/N values obtained are shown in Table 6-8. Reasonable %RSD values of <20% were obtained for most of these compounds, given the low loading of between 25-48 pg on the column, however a higher value of 35 % was obtained for DEHP. The S/N values of between 100 and 350 for most compounds suggest that the system would be able to detect lower amounts of these compounds. The higher value for benzene, combined with the higher mean peak area for this compound, may be explained by the background level of this compound being higher than the loading level. A significant background level is expected for benzene, with detectable amounts being found on conditioned tubes analysed using the MSD system (see Section C.4.1).

Table 6-8 Sensitivity study using carcinogen mix on TOF system

Compound	Mass on tube (ng)	Approximate mass on column (pg)	Extracted ion peak area (n=3)		RMS S/N (n = 3)
			Mean	%RSD	
Acrylonitrile	0.23	25	53,521	15.6	177
12-DCE	0.38	42	74,681	2.2	242
Benzene	0.28	31	2,284,900	19.4	1,771
Trichloroethylene	0.43	48	65,987	1.0	423
13-DCP	0.43	48	95,629	19.3	142
Benzyl chloride	0.37	41	152,135	11.0	324
o-Toluidine	0.32	35	47,410	12.5	193
o-Anisidine	0.35	39	17,976	11.3	102
4-Chloroaniline	0.28	31	25,786	11.7	187
DBP	0.40	44	459,056	7.9	347
DEHP	0.26	29	490,411	34.9	245

6.3.2.4 Study of blanks on TOF system

For many of the compounds in the check standard and carcinogen mixes it was observed that analysis of a blank tube or a tube spiked with just methanol at the low

split/high sensitivity settings also showed a peak. This was explored further by undertaking repeat tests of each constituent part of the process i.e. GC run, heating cold trap, analysis of an empty tube, analysis of blank (conditioned) tube and analysis of tube spiked with internal standard. Results of this blank study are shown in Table 6-9. No peaks were detected on initiating a GC run only. A small amount of benzene was observed on heating the TD cold trap; this did not increase if the trap was purged first. The benzene level was found to increase on analysis of an empty tube and some phenol and dibutyl phthalate were also then observed. The level of benzene, phenol and dibutyl phthalate increased significantly when a conditioned tube (whether or not spiked with the internal standard) was run and small amounts of some of the other compounds were also observed.

Results of this study suggest that the source of contamination is the sorbent (with some contribution from the methanol used as solvent for the internal standard). This shows the extra care required in keeping contamination to a minimum when analysing down to trace levels. Scrupulous conditioning of sorbent tubes is needed, though the tubes used in this study had been conditioned using the procedure described in Appendix A.4. The peak areas obtained for benzene, phenol and the two phthalates, for example, were a similar order of magnitude to those of the lowest standard. While a high background level was expected for benzene, further investigation is required for the other compounds to understand the limits achievable.

Table 6-9 Blank study on TOF system using low split ratio

Compound	Heat trap (n=2) [1]	Empty tube, desorb 8 min @ 50°C (n=7)	Empty tube, desorb 8 min @ 280°C (n=10)	Blank MS1 tube, desorb @ 280°C (n=9)	MS1 + internal standard (IS) (n=9)
	Mean response (Extracted ion peak area) (%RSD)				
MIBK	ND	ND	ND	ND	25,772 (11)
Toluene	ND	ND	4,891 (20)	206,920 (23)	507,056 (8.8)
Hexanal	ND	ND	15,761 (45)	ND	ND
Butyl acetate	ND	ND	ND	ND	31,172 (13)
m-Xylene	ND	ND	2,340 (40)	95,593 (41)	94,127 (16)
Cyclo-hexanone	ND	ND	ND	ND	ND
α-Pinene	ND	ND	ND	ND	ND
Phenol	ND	20,940 (11)	192,005 (55)	4,507,594 (39)	2,800,427 (17)
123-TMB	ND	ND	ND	12,261 (49)	24,245 (11)
Limonene	ND	ND	ND	3,276 (75)	14,896 (13)
4-PCH	ND	ND	ND	ND	ND
BHT	ND	ND	ND	ND	ND
n-Hexadecane	ND	ND	794 (37)	27,069 (71)	15,832 (22)
Acrylonitrile	ND	ND	ND	12,339 (18)	ND
12-DCE	ND	ND	ND	ND	ND
Benzene	56,048	115,235 (4.1)	136,047 (6.7)	1,877,974 (25)	1,563,992 (17)
Trichloro-ethylene	ND	ND	ND	ND	ND
13-DCP	ND	ND	ND	ND	ND
Benzyl chloride	ND	ND	ND	ND	ND
o-Toluidine	ND	ND	ND	ND	ND
o-Anisidine	ND	ND	ND	ND	ND
4-Chloro-aniline	ND	ND	ND	ND	ND
DBP	ND	ND	6,428 (16)	16,169 (6.0)	105,904 (25)
DEHP	ND	ND	ND	ND	261,174 (73)

[1] Similar result obtained after purging trap for 10 minutes before heating;
ND = not detected (no peak observed on quantitation within ChemStation)

6.3.2.5 Test of determination of carcinogens from re-collected tubes

Amounts of the check standard compounds and carcinogens determined in this test are given in Table 6-10. The recoveries for the majority of the carcinogens were similar for the freshly spiked tube, the tube re-collected from the analysis of a tube spiked with the carcinogen mix and for the tube spiked with the check standard mix and the carcinogen mix. For example, for 1,2-dichloroethane, 3.2 ng was found from the tube which had been analysed directly after spiking, whereas the amounts found from the two re-collected tubes were 3.3 and 2.9 ng. No 1,2-dichloroethane was detected from the tube resulting from the split effluent of that which had been spiked with the check standard mix only. So these compounds can be detected on re-collection in a relatively clean chromatogram containing only the check standard compounds. Amounts of benzene and the two phthalates were greater and detectable amounts of these compounds were also observed on the tube re-collected from analysis of the internal standard only and from that re-collected from analysis of the internal standard plus check standard mix. These findings suggest that use of re-collection is giving acceptable results for the compounds in the carcinogen mix, with the exception of benzene and the two phthalates.

6.3.3 Application to material emissions testing

The vinyl floor tile had been analysed previously (see Section 3.3.3.7) and found to emit significant amounts of a number of compounds. Five of these compounds were contained in the check standard mixture and these were quantified from the first desorption of these samples using the high level calibration for these compounds. The re-collected tubes were then analysed with the lower split setting to allow detection of the carcinogens. A chromatogram from the analysis of the re-collected tube is shown in Figure 6-2. This shows the major compounds emitted from the floor tile, i.e. butyl acetate, m-xylene, cyclohexanone, phenol and 2-ethylhexan-1-ol. The carcinogens appear at a trace level in this chromatogram, with the exception of benzene and the two phthalates which, as found in the previous experiment, were observed in greater amounts from re-collected tubes than from those analysed directly after spiking.

Table 6-10 Re-collection study on TOF system with standards using high split followed by low split

Tube loaded with:	IS		IS and carcinogen mix		IS and check standard mix	IS, check standard and carcinogen mix
Analysis undertaken:	**Low split analysis only**	**High split then low split**	**Low split analysis only**	**High split then low split**		
Compound	**Amount determined (ng on tube)**					
Check standard compounds – analysed with high split						
MIBK		ND		ND	214	251
Toluene		ND		ND	211	211
Hexanal		ND		ND	215	231
Butyl acetate		ND		ND	225	248
Cyclohexanone		ND		ND	236	273
Phenol		ND		ND	178	181
123-TMB		ND		ND	269	273
4-PCH		ND		ND	312	295
BHT		ND		ND	272	260
n-Hexadecane		ND		ND	289	317
Carcinogens – analysed with low split						
Acrylonitrile	ND	ND	1.4	1.3	ND	0.6
12-DCE	ND	ND	3.2	3.3	ND	2.9
Benzene	ND	1.3	1.0	3.9	1.1	3.1
Trichloroethylene	ND	ND	2.8	2.9	ND	2.4
13-DCP	ND	ND	2.5	1.7	ND	2.3
Benzyl chloride	ND	ND	2.4	1.9	ND	2.2
o-Toluidine	ND	ND	1.8	1.8	ND	1.5
o-Anisidine	ND	ND	2.0	1.8	ND	1.6
4-Chloroaniline	ND	ND	2.0	1.8	ND	1.6
DBP	ND	2.5	2.0	6.3	2.2	8.4
DEHP	ND	9.3	4.2	7.5	5.9	10.3

ND = Not detected

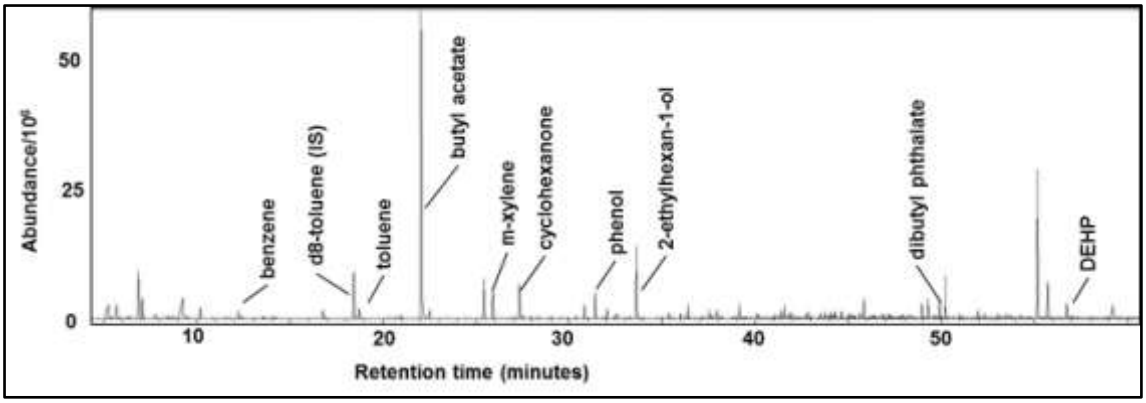

Figure 6-2 Chromatogram of air sample from an emissions test spiked with approximately 3 ng of the carcinogen mix and analysed on TOF MS system with re-collection

Concentrations of the check standard compounds and amounts of the carcinogens determined are shown in Table 6-11. As with the previous experiment, similar recoveries were found for the majority of the carcinogens from the freshly spiked tubes and those re-collected from the emission samples which had been spiked with the carcinogen mix. Amounts of benzene and the two phthalates were again greater in the re-collected spiked tubes and these compounds also appeared in the re-collected tubes which had not had carcinogen mix added. The other compounds were not observed in analyses where they had not been added. Therefore, this demonstrates the potential of the high/low sensitivity method for determination of low levels of some carcinogens in the presence of greater amounts of other compounds. Further repeatability tests and additional tests of performance with further complex chromatograms is desirable. There does, however, appear to be a problem in the determination of a few compounds (benzene and the two phthalates) using re-collected tubes.

Table 6-11 Re-collection study on TOF system with emission samples using high split followed by low split

	Controls				Air sample from FLEC			
					3 days		21 days	
Tube loaded with:	**IS**		**IS and carcinogen mix**		**IS**	**IS and carcinogen mix**	**IS**	**IS and carcinogen mix**
Analysis undertaken:	**Low split analysis only**				**High split then low split**			
Check standard compounds – analysed with high split, Concentration (μg m^{-3})								
MIBK					ND	ND	ND	ND
Toluene					2.6	2.8	2.8	2.2
Hexanal					ND	ND	ND	ND
Butyl acetate					70	66	37	40
m-Xylene					5.0	5.0	3.7	3.7
Cyclohexanone					10	10	8.0	8.2
Phenol					4.7	4.9	4.4	4.8
123-TMB					ND	ND	ND	ND
4-PCH					ND	ND	ND	ND
BHT					ND	ND	ND	ND
n-Hexadecane					ND	ND	ND	ND
Carcinogens – analysed with low split, amount determined (ng on tube)								
Acrylonitrile	ND	ND	1.2	1.2	ND	0.6	ND	1.0
12-DCE	ND	ND	2.9	2.9	ND	3.1	ND	3.0
Benzene	ND	ND	1.5	1.6	2.5	6.3	1.9	5.5
Trichloro-ethylene	ND	ND	2.3	2.4	ND	2.4	ND	2.4
13-DCP	ND	ND	2.3	2.5	ND	2.9	ND	2.9
Benzyl chloride	ND	ND	2.0	2.3	ND	2.5	ND	2.6
o-Toluidine	ND	ND	1.4	1.7	ND	1.6	ND	1.6
o-Anisidine	ND	ND	1.7	1.8	ND	1.5	ND	1.6
4-Chloroaniline	ND	ND	1.6	1.9	ND	1.3	ND	1.5
DBP	ND	ND	1.9	5.1	6.2	11.5	6.6	15.2
DEHP	2.4	0.4	4.3	9.4	12.7	24.8	6.5	45.7

6.3.4 Comparison with previous studies

The BenchTOF-dx is a recently introduced instrument and a search of the literature has identified few reported studies of its application to the measurement of VOCs in air. One group (Leppert et al., 2012) has reported use of the instrument to determine chemical warfare agents and five simulants in air. They estimated the limit of detection of the simulant compounds to be 20-150 pg, which was two to three orders of magnitude lower than the values found for these compounds using a GC with full scan quadrupole MS. While it is difficult to compare the actual values, the present work suggests that a similar improvement in sensitivity may be achieved for the compounds investigated as being of concern in material emissions. Kim and Kim (2012) used an analytical system comprising a BenchTOF-dx MS to determine VOCs in ambient air. They investigated 19 compounds, five of which were included in the present study. They also found a considerable enhancement in sensitivity compared to use of a standard MS system. Significant responses were observed, however, for eight of their target compounds, including benzene, toluene and m-xylene which were also examined in the present study, on analysis of blank sorbent tubes. They recommended stringent conditioning of the analytical system and sampling tubes, together with sufficient blank runs in order to minimise and quantify the blank levels.

6.4 Conclusions

The analytical system incorporating a TOF MS was set up with parameters optimised for the testing of emissions from materials. The instrument was shown to detect target compounds for material emissions testing at a significantly lower level than possible using a standard MS in full scan mode. The potential of a high/low sensitivity analysis to determine analytes occurring across a wide concentration range has been demonstrated, with some issues with the amounts of benzene and phthalates found on re-collection. This appears to be associated with the background level of these compounds which increases on re-collection. It is a possibility that this is caused by the presence of some contamination in the flow path of the TD. Nevertheless, good results were obtained for other compounds tested. To confirm the potential of the method, further tests are required using a range of complex emission profiles.

7 INVESTIGATION INTO THE USE OF NEW COMPOUND IDENTIFICATION SOFTWARE TO DETERMINE TARGET COMPOUNDS IN MATERIAL EMISSIONS

7.1 Introduction

As discussed in Section 2.5, the determination of extensive lists of target compounds in the emissions from materials are required, to satisfy various labelling schemes. These lists of chemicals are also the subject of frequent revision with improved knowledge of effects on health and with progress towards harmonisation of different schemes. Processing of data produced by the analytical system to confirm the presence and amounts of each compound on a target list is a time consuming process. Determination of trace levels of carcinogens within a complex chromatogram is particularly challenging. The AgBB scheme, for example, currently contains a list of 176 chemicals with LCI (lowest concentration of interest) values and additionally includes the requirement to determine a separate list of carcinogens to a low level. Processing involves viewing the quantitation results for each compound within ChemStation (or other software package employed) and deciding if the correct peak has been assigned to that compound and if so if it has been integrated correctly (i.e. the baseline drawn in the right place). The possibility of automating this procedure has the potential to save time, which would be of particular benefit to laboratories providing routine analysis for product producers. A more automated procedure would also lower costs as less specialised staff would be required.

TargetView compound identification software, which was introduced in Section 1.5.5, has been developed to provide automated determination of target compounds within a complex chromatogram. This involves a several step process employing background subtraction, followed by spectral deconvolution, after which the deconvolved spectra are matched against a library containing spectra of compounds of interest using chemometric data analysis. The final objective of this project was therefore to investigate the application of TargetView software to the determination of VOCs emitted from materials.

The initial focus was the use of the software package to identify target compounds in a chromatogram. The package was, however, continuing to be developed during the course of the project to improve its quantitative aspects. Later work therefore involved a quantitative comparison of results obtained by manual processing of data files within ChemStation software and using TargetView. This aspect of the project involved collaboration with personnel from Markes International. Advice was received from Markes on adjustments in settings in order to improve the results obtained and examples of poor comparability remaining after optimisation were reported back. Proposed upgrades to the software, developed with the aim of improving quantitative aspects of the software were provided for testing. Some of these upgrades were supplied in advance of them becoming commercially available. This resulted in a number of different versions of the software being trialled during the course of the work.

7.2 Methods

7.2.1 Qualitative work

Using version 1.0 of TargetView, a library was created by importing the ChemStation user generated library built up of spectra of target analytes which had been determined on the TD-100/GC/MSD system (at the time 100 compounds). The library also included retention times for these compounds on the system. The software was applied to the identification of target analytes in chromatograms obtained from tests of the four materials undertaken during the study of emissions using the μ-CTE and a Nalophan bag (Section 3.3.2). The numbers of the target compounds found using this technique were compared with those identified in the chromatograms by manual processing using ChemStation software. For this investigation default processing parameters were used within TargetView (peak width of 6 seconds, window width limit [ΔRT] of 10 seconds, minimum matching coefficient of 0.75 and 'penalty method' automatic).

7.2.2 Quantitative work

In order to investigate the use of TargetView for quantitation, further target libraries were created each containing small selections of compounds to be tested. During these studies the results obtained from optimisation of processing parameters were

investigated and different versions of the software were applied as they became available. Initially two libraries were prepared containing the 11 ‘check standard’ compounds (see Section 1.4.1). One of these libraries contained spectra generated on the TD-100/GC/MSD system, whilst the spectra in the other were extracted from the NIST library. The two versions were prepared to investigate whether the sets of spectra gave any difference in results and if so which would prove more reliable. These libraries were applied to process data obtained from the QC tubes used to demonstrate the performance of the analytical system (see Appendix C.4).

Results obtained using TargetView were compared to those obtained by processing the data within ChemStation. Initially this involved comparison of responses obtained for a characteristic ion for each compound using the two packages (peak areas in the case of ChemStation and peak sums in the case of TargetView). Later calibration curves were prepared for these compounds in Microsoft Excel using the extracted ion peak sum values generated by processing calibration standard chromatograms using TargetView. Amounts of each compound calculated using the software could then be compared with amounts determined using ChemStation.

In further studies, TargetView libraries were created for significant compounds observed in the emissions tests of wall covering materials (Section 3.3.3) and from the samples of window and door materials tested previously (Section 3.3.1). These used spectra generated on the TD-100/GC/MSD system, with the exception of one compound, methylcyclobutane (MCB), for which no chemical standard was available so the spectrum obtained from the NIST library was used. Calibration curves were again prepared in Excel using the TargetView extracted ion peak sum values generated by processing calibration standard chromatograms. For each of these compounds the same ion was used for quantification as had been used to process that compound in ChemStation. MCB was semi-quantified using the TargetView and ChemStation total ion chromatogram (TIC) responses for toluene.

The final part of this objective involved comparison of amounts of compounds found using the two software packages for chromatograms generated using the analytical system incorporating the BenchTOF-dx MS. For this instrument the native files having an ‘.lsc’ extension were used for processing within TargetView, rather than using the

files having a '.d' extension, which the data is converted to for processing within ChemStation. A TargetView library was created for the 11 compounds in the mixture of carcinogens (see Section 6.2.2) by extracting spectra from the NIST library. Calibration curves were prepared in Excel using the TargetView extracted ion peak sum values generated by processing calibration standard chromatograms obtained on this instrument for these compounds. The calibration curves were then applied to the quantification of these compounds in tubes analysed using this instrument in tests described in Section 6.3.3.

7.3 Results and Discussion

7.3.1 Application to qualitative analysis of MSD data

The number of the 100 target analytes detected in sample and control chromatograms from emissions tests of Material A (a carpet tile) using the μ-CTE and the Nalophan bag method and processing manually with ChemStation and automatically with TargetView are shown in Table 7-1. The two techniques found broadly the same target compounds on a chromatogram resulting in similar total numbers of the target compounds, although a few compounds identified using manual processing were not found using TargetView and vica versa.

Table 7-1 Number of target compounds emitted from Material A identified from different screening methods using ChemStation and TargetView for processing

	Bag, 40 °C		**Bag, 60 °C**		**μ-CTE, 40 °C**		**μ-CTE, 65 °C**	
	Chem-Station	**Target-View**	**Chem-Station**	**Target-View**	**Chem-Station**	**Target-View**	**Chem-Station**	**Target-View**
Sample	31	32	40	33	17	20	27	26
Control	10	14	10	12	3	9	7	13

The number of the 100 target analytes detected for Materials B-D using the bag method at 40 °C is shown in Table 7-2. The two processing methods are again seen to detect broadly similar numbers of the compounds in a particular chromatogram, with neither of the methods consistently detecting a significantly greater number than the other.

Table 7-2 Number of target compounds emitted from Materials B-D using bag method at 40 °C and processing with both ChemStation and TargetView (v1.0)

	Material B		Material C		Material D	
	Chem-Station	Target-View	Chem-Station	Target-View	Chem-Station	Target-View
Sample	34	33	13	21	37	34
Control	9	15	12	14	16	16

This study had used the initial version of TargetView with default settings. The possibility of increased numbers of target compounds being identified by optimisation of the settings or reprocessing of the data using an updated version of the software was not investigated. Any differences in the limits of detection for the two processing techniques could also explain differences in numbers of compounds identified. Quantification of identified compounds would highlight this, so further studies undertaken using TargetView incorporated quantitation.

7.3.2 Application to quantitative analysis of MSD data

7.3.2.1 Processing of data from QC tubes

Initially the responses obtained for each compound included in the daily QC tubes were compared using ChemStation and TargetView (version 1.0). The TargetView library formed using spectra of the 11 compounds analysed on the same instrument was used for this study. For some of the compounds fairly consistent responses were observed, while for others occasionally a much smaller value was recorded using TargetView or the peak was not found at all. In these cases the peak had appeared normal in the chromatogram and gave an appropriate response in ChemStation. The findings for 10 QC tubes processed using ChemStation and TargetView are shown in Table 7-3. (These are responses for a characteristic ion for each compound, but note that the ‘peak sum’ values given by TargetView are not expected to be the same as the peak area values produced by ChemStation). For most of the compounds a somewhat higher %RSD was observed using TargetView (version 1.0) than using ChemStation and in some cases the %RSD was dramatically larger, e.g. cyclohexanone for which an RSD of 90% was recorded using TargetView compared with that of 6.7% using ChemStation.

Application of version 1.2 of the software, for which the manufacturer claimed an improved deconvolution algorithm, showed much improvement. For the majority of the compounds a similar variability in the responses was seen for both software packages, suggesting that this is due to variations in instrument response. For a few of the compounds, however, the variability was somewhat higher using TargetView and for one compound, 4-phenylcyclohexene (4-PCH), a very high RSD (53 %) was obtained. On examination this was found to be due to a very low response being obtained for two of the 10 samples.

Table 7-3 Initial quantification study of ten QC tubes using ChemStation and TargetView

Compound	ChemStation		TargetView v1.0		TargetView v1.2	
	Mean Peak Area [1]	**%RSD**	***Mean Peak Sum*** [1]	**%RSD**	***Mean Peak Sum***	**%RSD**
d8-Toluene	*2,259,187*	10.4	*831,329*	47.4	*1,362,568*	16.1
n-Hexane	*1,712,651*	7.8	*891,800*	24.8	*1,083,109*	7.9
MIBK	*3,811,034*	5.5	*2,139,300*	13.9	*2,354,025*	5.1
Toluene	*5,025,993*	4.8	*2,256,900*	45.3	*3,070,116*	11.5
Hexanal	*1,702,695*	10.1	*708,318*	47.7	*1,076,457*	17.9
Butyl acetate	*4,675,074*	6.5	*1,934,900*	43.8	*2,742,178*	21.3
Cyclohexanone	*3,255,003*	6.7	*943,713*	90.1	*2,055,199*	6.4
Phenol	*3,617,501*	11.3	*1,707,500*	46.1	*2,258,962*	10.7
123-TMB	*5,284,006*	4.1	*3,010,200*	24.2	*3,337,164*	4.1
4-PCH	*10,009,295*	6.8	*5,664,800*	35.9	*5,000,760*	53.0
Butylated hydroxytoluene (BHT)	*3,594,451*	5.9	*2,270,080*	5.7	*2,276,075*	5.9
n-Hexadecane	*6,983,011*	9.1	*3,851,300*	21.5	*4,416,945*	9.2

[1] note that peak area and peak sum values are not directly comparable

Chromatograms from duplicate analyses of seven dilutions of the QC compounds containing between 2.5 and 2,500 ng of each compound on a tube were processed using TargetView in order to prepare calibration curves using this method. This test used version 1.3 of the software, which was the first commercially released upgrade and was advertised as having additional and improved functionality over version 1.0 (extent of improvement over version 1.2 being less clear). From the 14 tubes one anomalously low

value was found for the internal standard (IS) [d8-toluene] which had about one half of the expected peak area. The same occurred, with a different tube, for cyclohexanone. Three tubes were also found to give very low values for 4-PCH. Repeating the processing using the target library containing spectra extracted from the NIST database gave correct values for the three 4-PCH peaks, but not for the other two compounds. Using the results from the NIST extracted library, and excluding the two anomalous values, curves for each compound were prepared in Excel, using ratios to the d8-toluene 98 ion peak sum values in each case. The results obtained are shown in Table 7-4; together with the details from calibration curves produced using the same data files in ChemStation. The same linear range was found for all 11 compounds using both processing methods, while the correlation coefficients were also all very good.

Table 7-4 Calibration data for MSD system obtained using ChemStation and TargetView processing

Compound	ChemStation				TargetView (v1.3)			
	Gradient	Intercept	Correlation coefficient (r^2)	Linear range (ng)	Gradient	Intercept	Correlation coefficient (r^2)	Linear range (ng)
n-Hexane	0.556	0.151	0.998	2.5-1000	0.572	0.174	0.998	2.5-1000
MIBK	0.834	0.120	0.999	2.5-1000	0.845	0.139	0.998	2.5-1000
Toluene	1.085	0.143	0.999	2.5-1000	1.105	0.191	0.999	2.5-1000
Hexanal	0.340	0.064	0.999	2.5-1000	0.345	0.092	0.998	2.5-1000
Butyl acetate	0.925	0.160	0.998	2.5-1000	0.895	0.231	0.996	2.5-1000
Cyclohexanone	0.593	0.061	0.999	3.0-1000	0.602	0.083	0.999	3.0-1000
Phenol	0.679	0.060	0.999	2.5-1000	0.694	0.070	0.999	2.5-1000
123-TMB	1.007	0.118	0.999	2.5-1000	1.029	0.147	0.999	2.5-1000
4-PCH	1.711	0.023	0.999	3.0-300	1.740	0.113	0.999	3.0-300
BHT	0.717	0.058	0.999	2.5-300	0.737	0.038	0.999	2.5-300
n-Hexadecane	1.277	0.094	0.998	2.5-300	1.296	0.154	0.996	2.5-300

The resulting TargetView calibration factors were applied to the peak sum values obtained from on-going QC check tubes. For most compounds the % recoveries

obtained using TargetView mirrored those obtained using ChemStation. As an example, the % recoveries for toluene from 16 QC tubes analysed over a period of two months and processed using the methods are shown in Figure 7-1. The mean % recovery obtained using ChemStation was was103.1 % (RSD 6.7 %) and that for TargetView 101.5 % (RSD 8.8 %). A similar finding was observed for 4-PCH (Figure 7-2), with the exception of one instance where the peak was not seen by TargetView.

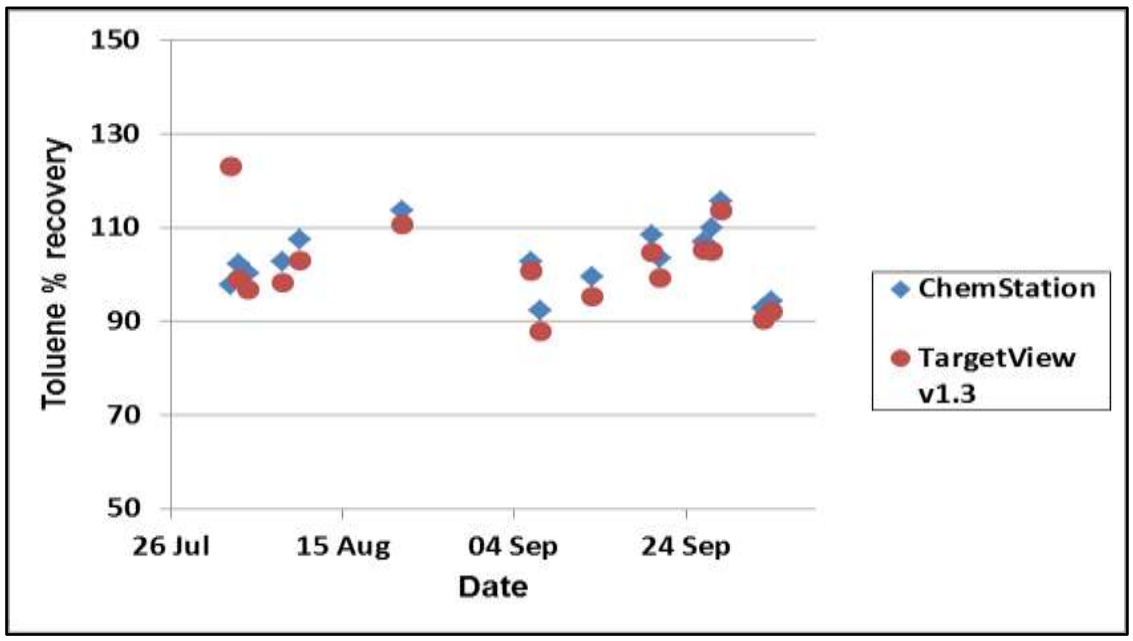

Figure 7-1 Percentage recovery for toluene in QC tubes using ChemStation and TargetView v1.3

An investigation of settings with the potential for optimisation was undertaken in an attempt to identify the missing 4-PCH peak. Reducing the window width limit (ΔRT) from 10 to 5 seconds was found to allow the peak to be identified and quantified with an appropriate peak sum value (shown by the green triangle in Figure 7-2). Increasing the 'minimum signal of most abundant ion' (threshold) value (from 400 to 5,000) was also found to recognise the peak, but this setting could risk the loss of target analytes that are present in the chromatogram in low amounts.

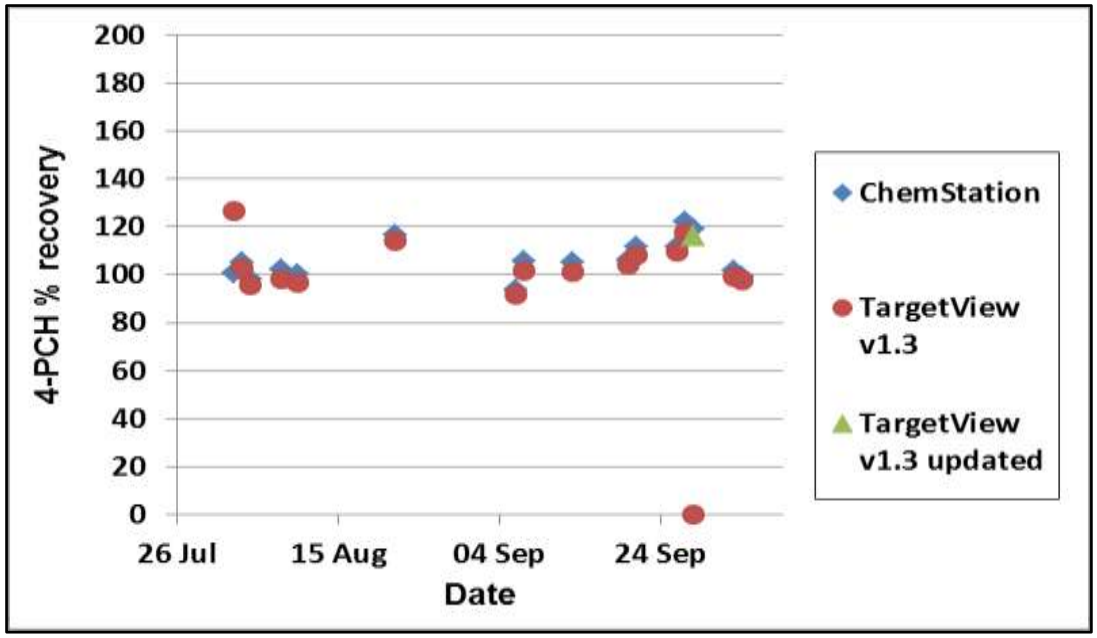

Figure 7-2 Percentage recovery for 4-PCH in QC tubes using ChemStation and TargetView v1.3

Using the narrower ΔRT value, the 4-PCH was found using both of the target libraries. A likely explanation of the effect of adjustment of these parameters is that the chemical used to calibrate for this compound contains, as an impurity, a small amount of an isomer which elutes close to the compound of interest. If the isomer happens to give a better spectral match against the library than the other compound it will be selected in its place. Narrowing the ΔRT value removes the possibility of the wrong isomer being selected as does increasing the threshold value. The different result obtained in some instances from use of the two libraries is thought to be due to slight differences in the spectra stored in the libraries meaning that sometimes one isomer received a higher match and sometimes the other.

The chromatogram from one of the calibration tubes in which the cyclohexanone peak was only partially picked up by TargetView was also investigated to see whether a similar adjustment of the processing parameters could give an improved result. In this case no combination of parameters was found to increase the peak sum value. On investigation of the data it was observed that the peak was of uneven shape [Figure 7-3 (a)] which might cause the software to see it as two peaks and thus explain a peak sum

value of about one half of the expected value. The peak shape can be improved by using peak smoothing filters, such as Savitsky-Golay smoothing which is available within ChemStation. Peak smoothing has been used in spectrometry to reduce instrumental noise and therefore improve the accuracy of data extraction from the spectra for many years (Bromba and Ziegler, 1981). The cyclohexanone peak shown in Figure 7-3(b), demonstrates that smoothing within ChemStation can give an improved peak shape. Application of version 1.4 of TargetView, which included more rigorous peak smoothing (among other enhancements), was found to give a more accurate representation of the size of the peak.

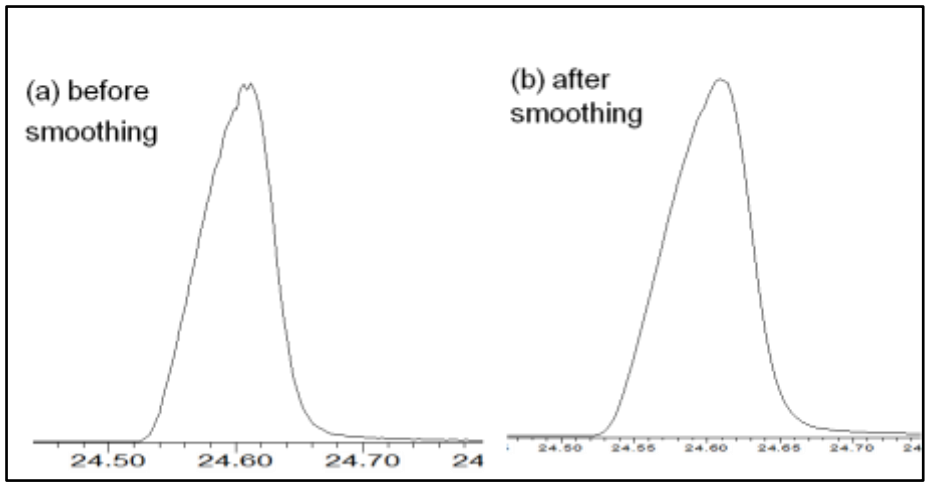

Figure 7-3 Cyclohexanone peak showing effect of smoothing by ChemStation software

The chromatograms from the 16 QC tubes examined above were re-processed using version 1.4 of TargetView and found a closer correspondence between the two methods, possibly as a result of the greater peak smoothing. The % recoveries for toluene using the ChemStation and TargetView v1.4 are shown in Figure 7-4. A mean recovery of 103.4 % (RSD 6.8 %) was found using this version of TargetView, compared to the value of 103.1 % (RSD 6.7 %) found using ChemStation; for 4-PCH the values obtained were 106.0 % (RSD 7.4 %) using TargetView and 106.2 % (RSD 7.5 %) using ChemStation.

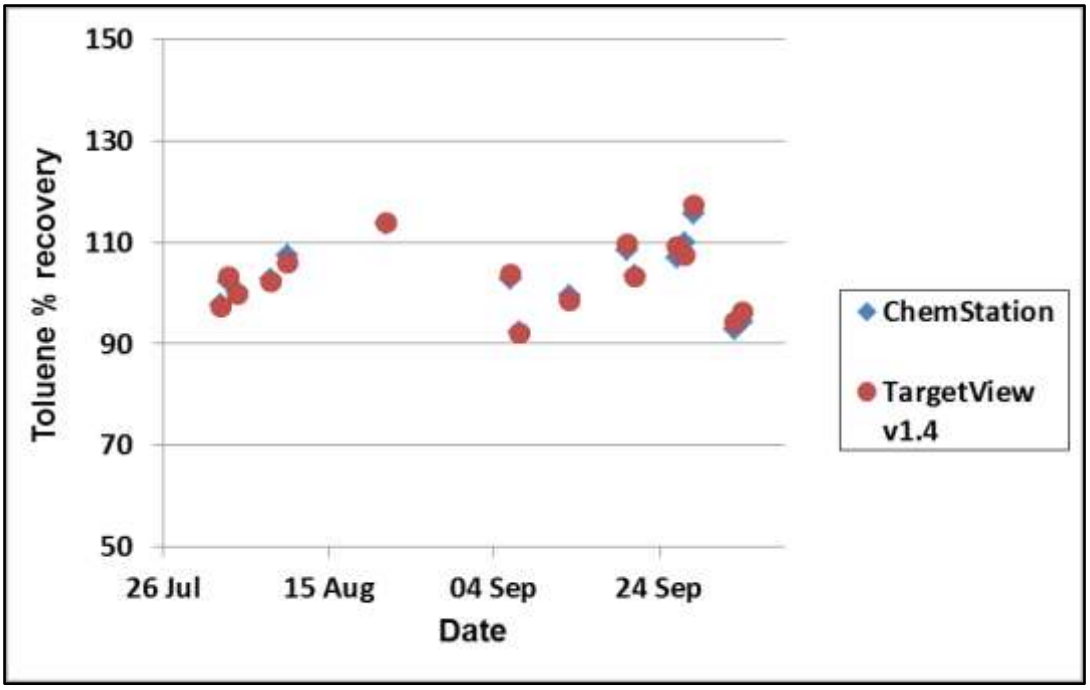

Figure 7-4 Percentage recovery for toluene in QC tubes using ChemStation and TargetView v1.4

7.3.2.2 Processing of material emissions data

To test the performance of TargetView for processing the wall covering test data, calibration curves were prepared within TargetView for nine compounds found in significant amounts in these emissions. An example of a chromatogram of the standard mixture for these compounds is shown in Figure 7-5. Calibration curves for seven of the compounds (including separate responses for the two Texanol isomers) are shown in Figure 7-6. The other two compounds studied, n-decane and n-dodecane, gave responses very similar to those for n-undecane and 2-butoxyethanol respectively. Very good linear responses were achieved for all the compounds, with correlation coefficients of 0.994 or greater being obtained in each case. For three of the compounds, hexanal, 2-ethylhexanoic acid and Texanol, the lowest calibration level which had been quantified using ChemStation was not observed using TargetView. A slightly higher limit of detection was therefore being achieved for some compounds with the version of the software used (v1.4). For comparison of the quantification of sample chromatograms using the two processing techniques the same quantification range was used in each case.

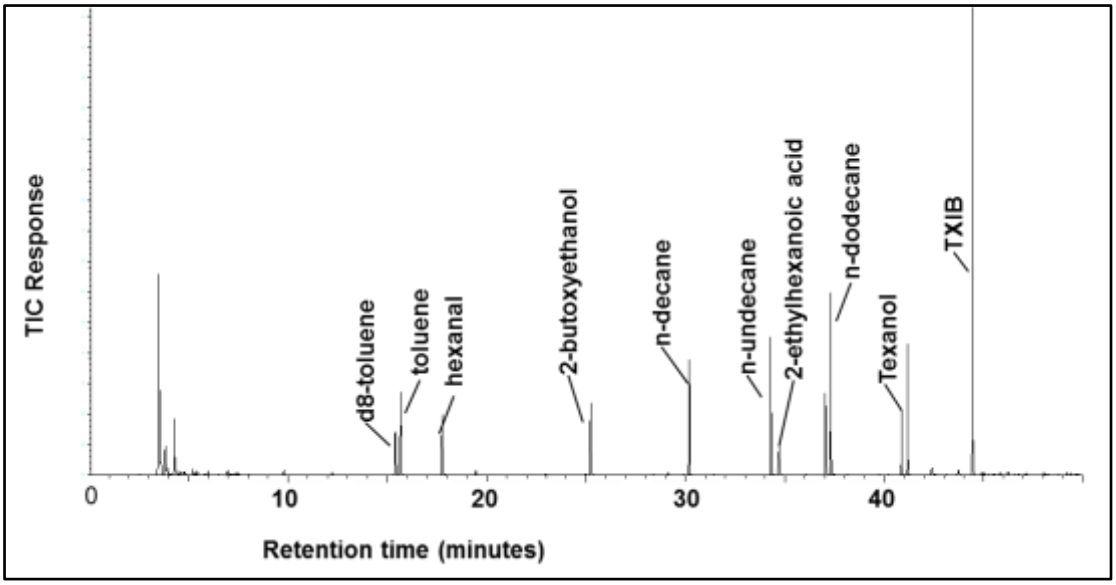

Figure 7-5 Chromatogram of nine compounds found in significant amounts in emissions from wall coverings

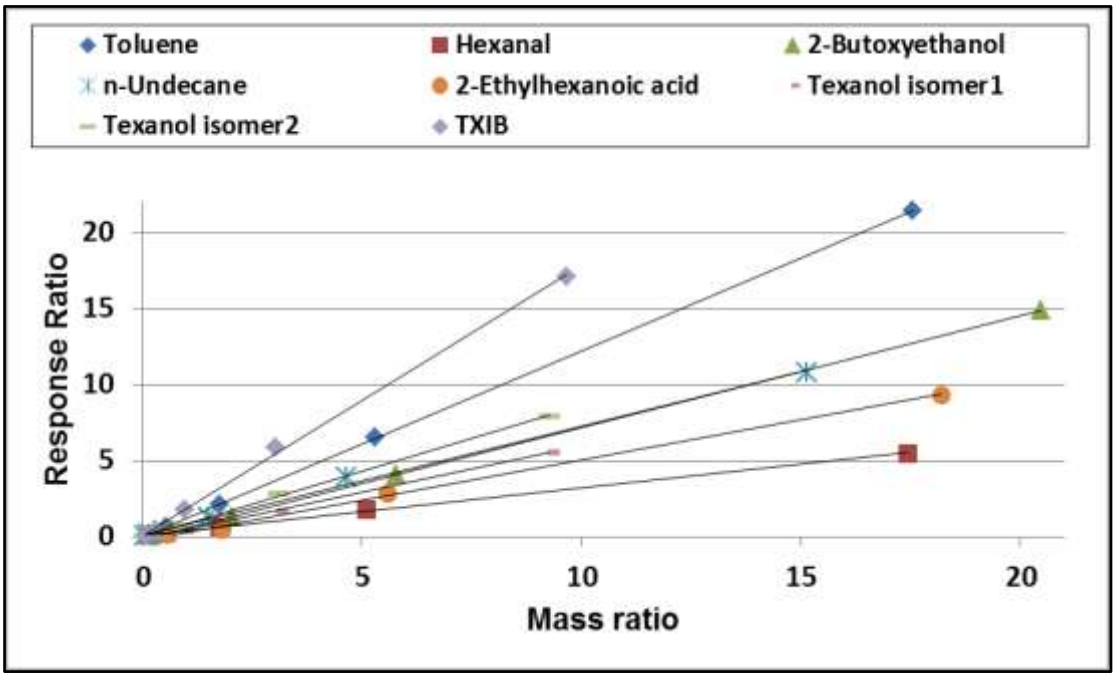

Figure 7-6 Calibration curves obtained using TargetView (v1.4) for seven compounds occurring in significant amounts in emissions from wall coverings

22 chromatograms from the wall covering material emissions tests were examined using the two techniques. These were selected to cover as broad as possible a concentration range for the nine compounds chosen for comparison. Figure 7-7 shows correlations of the amounts obtained using ChemStation and TargetView to process the chromatograms. Excellent correlations were obtained across the whole concentration range for eight of the compounds, with gradients between 0.90 and 1.05 and $r^2 \geq 0.994$. Quantification using TargetView for these compounds would therefore have given an equivalent result to that obtained using ChemStation. The remaining compound studied, 2-ethylhexanoic acid, shown in Figure 7-7(i), gave a poorer correlation. If values of around 150 ng and lower only were plotted however, Figure 7-7(j), these were found to have a gradient of 1.16 and r^2 of 0.997. This result could be explained by the very poor peak shape given by this compound on the DB-5 column due to its high polarity. It therefore proves a challenge for the software to determine the limits of the peak especially as the size of the peak increases. Increasing the peak width setting was investigated but was not found to improve the correlation.

Quantification of 2-ethylhexanoic acid within ChemStation was also not straightforward, with manual re-integration being required for the majority of chromatograms. Strictly, this compound falls outside the scope of ISO 16000-6:2011 which is applicable to the measurement of non-polar and slightly polar VOCs. Reliable quantification of this compound would therefore require a different GC column.

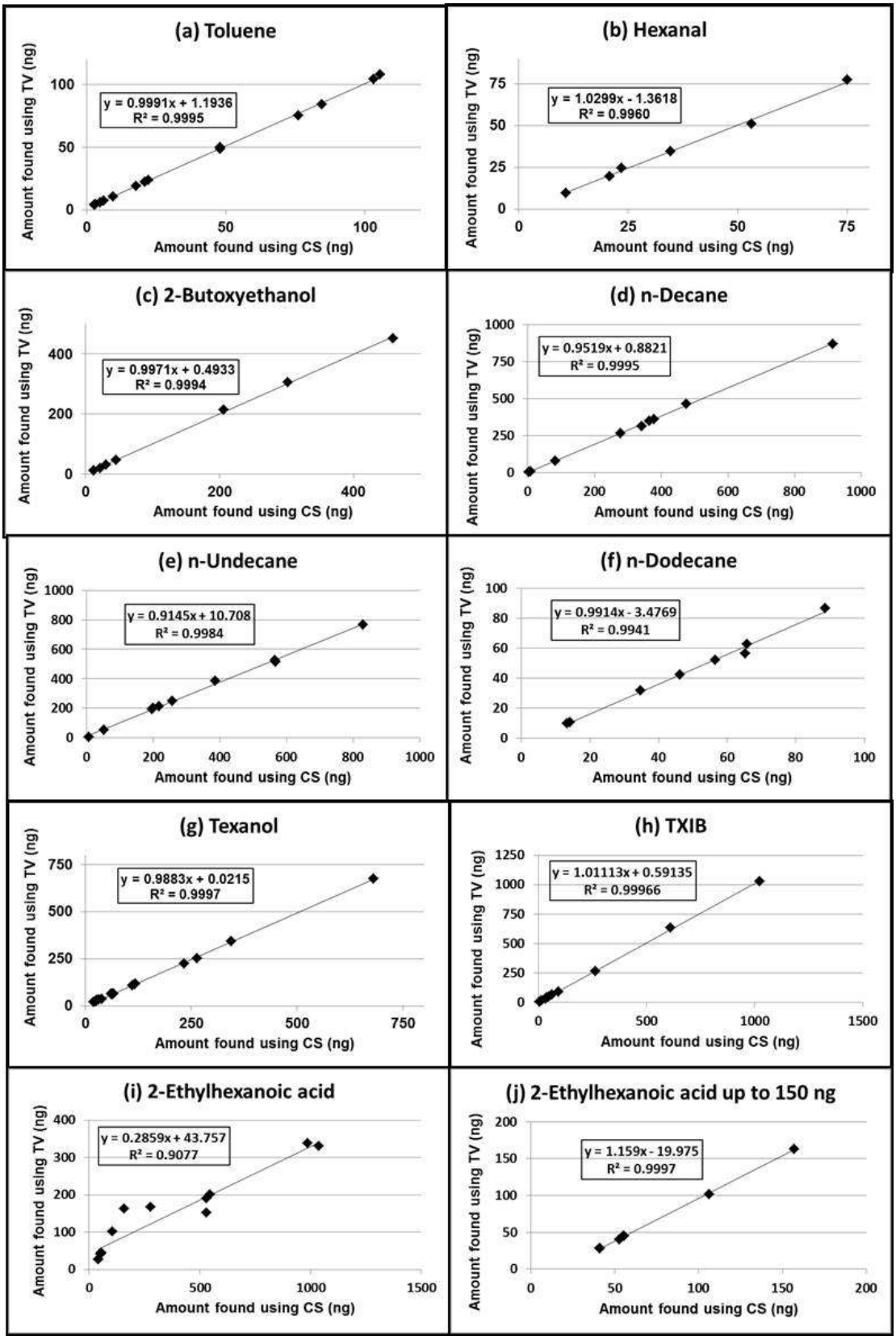

Figure 7-7 Amounts of VOCs found in wall covering emissions using ChemStation (CS) and TargetView (TV) (v1.4) processing

For the door and window materials, 13 compounds found in the emissions were selected for study. 40 chromatograms were examined using TargetView (version 1.4); each of the selected compounds had been identified in at least 14 of these using ChemStation. With TargetView the same compounds were found in each chromatogram as had been found with ChemStation. One chromatogram gave values for all compounds which were about double those obtained in ChemStation. This was thought to be due to the d8-toluene peak having an uneven shape, resulting in it being underestimated, and hence amounts for target analytes being over-reported. [This file was not included in the data analysis, though since this work was undertaken the chromatogram was examined with version 2.0 of the software (TargetView Plus) and the peak was quantified correctly].

The correlations between the two processing methods for ten of the selected compounds are shown in Figure 7-8. These all gave very good results across a wide range of tube loadings, with gradients between 0.98 and 1.03 and $r^2 \geq 0.997$. (Note that the linear range for some of these compounds was extended by the use of a range of split flows during desorption; the split was set according to the expected loading on the tube). Methylcyclobutane (MCB), which had been semi-quantified using the total ion chromatogram (TIC) responses for toluene, Figure 7-9(a), also showed an excellent correlation between the two methods. A further compound studied, n-dodecane [Figure 7-9(b)], showed a poorer correlation between the two methods owing to a lower result being obtained with TargetView than had been found using ChemStation for a number of the chromatograms. A chromatogram of this material showed this compound to occur in an area of overlapping peaks (see Figure 3-1) so it is possible that an interfering compound is resulting in an overestimate of the amount recorded by ChemStation. One test was undertaken in which this compound was reprocessed in both ChemStation and TargetView using m/z 85 as the quantification ion instead of 57, but this did not result in an improved correlation. A problem with n-dodecane, as for hydrocarbons generally, is that its spectrum is composed of ions which are common to many different compounds. This compound had also been investigated in the study of emissions from wall coverings, where a good correlation between the methods was achieved, and the observation that in the chromatograms from these materials the peak occurs in an area of less overlap (see Figure 3-19) supports the theory that the discrepancy is caused by an interfering peak.

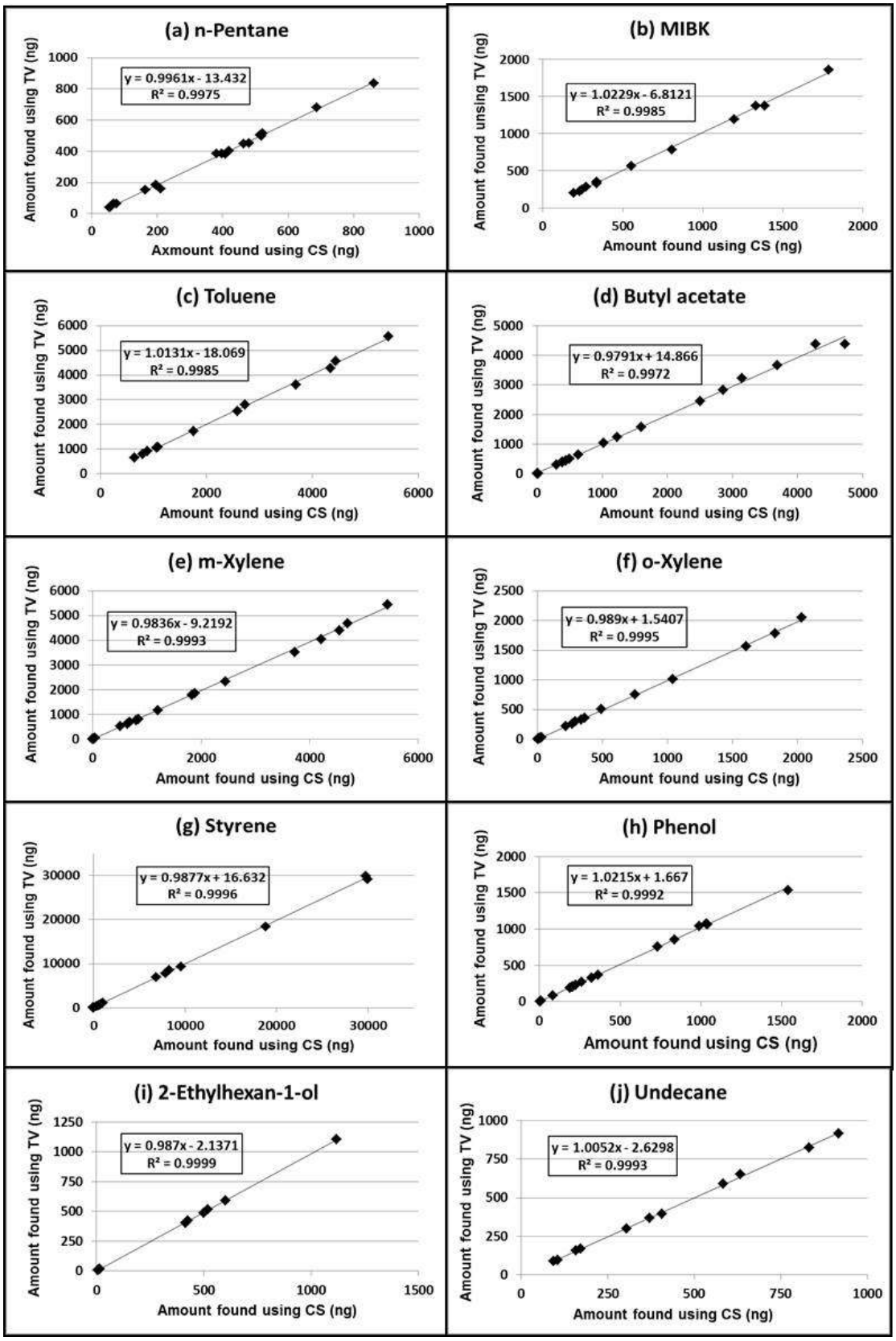

Figure 7-8 Amounts of 10 VOCs found in door and window emissions using ChemStation (CS) and TargetView (TV) processing

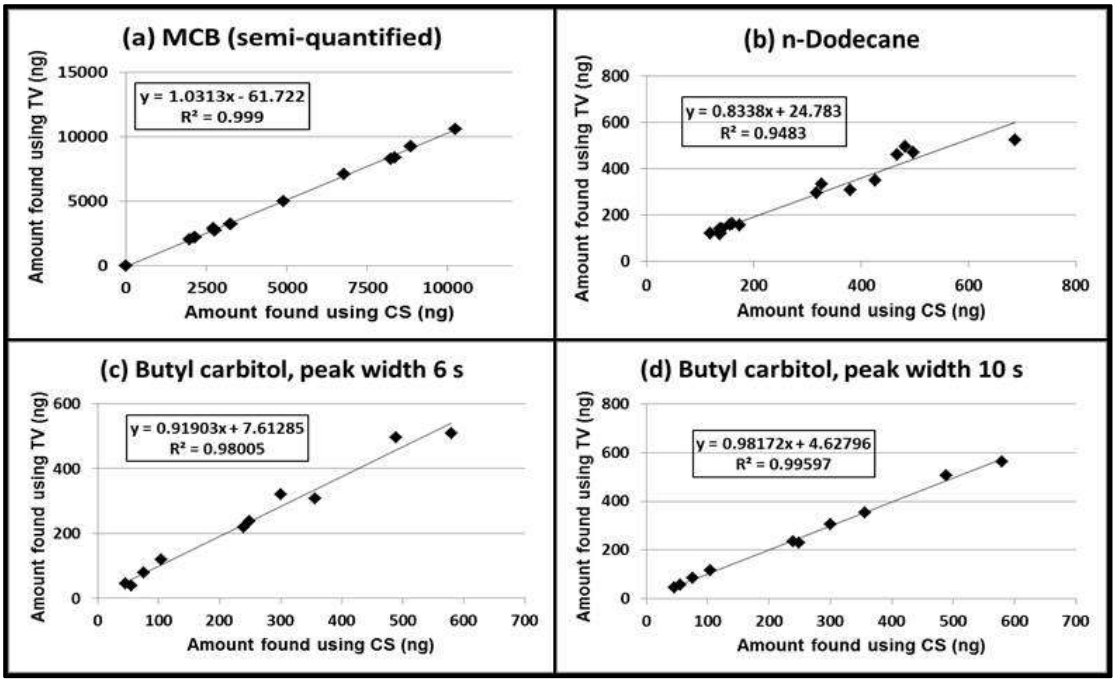

Figure 7-9 Amounts of three further VOCs found in door and window emissions using ChemStation (CS) and TargetView (TV) processing

The remaining compound studied, butyl carbitol [or 2-(2-butoxyethoxy)ethanol], also showed more variable results, Figure 7-9(c). The effect of increasing the peak width setting was investigated, as this compound elutes as a rather broad peak on the GC column, and, in this instance, resulted in an improved correlation, Figure 7-9(d), with the gradient being increased from 0.92 to 0.98 and r^2 from 0.98 to 0.996.

7.3.3 Application to TOF data

Chromatograms from duplicate analyses using the TOF system of six dilutions of the mixture of 11 carcinogens (see Section 6.2.2) containing between 0.1 and 23-43 ng of each compound on a tube were processed using TargetView version 2.0. The results obtained were used to produce calibration curves for these compounds. Peaks were detected for all the compounds across the concentration range examined and the gradients, intercepts and correlation coefficients were very similar to those obtained using ChemStation in each case (Table 7-5).

Table 7-5 Calibration data for TOF system obtained using ChemStation and TargetView processing

Compound	ChemStation				TargetView (v2.0)			
	Gradient	Intercept	Correlation coefficient (r^2)	Concentration range (ng)	Gradient	Intercept	Correlation coefficient (r^2)	Concentration range (ng)
Acrylonitrile	0.422	-0.001	0.999	0.1-23	0.417	-0.001	0.999	0.1-23
1,2-Dichloro-ethane	0.411	-0.002	0.999	0.1-38	0.409	-0.003	1.000	0.1-38
Benzene	1.327	0.052	0.999	0.1-28	1.355	0.045	0.999	0.1-28
Trichloro-ethylene	0.354	-0.002	0.999	0.1-43	0.354	-0.003	0.999	0.1-43
1,3-Dichloro-propan-2-ol	0.644	-0.008	0.998	0.1-42	0.632	-0.009	0.998	0.1-42
Benzyl chloride	0.974	-0.005	0.999	0.1-38	0.981	-0.008	0.999	0.1-38
o-Toluidine	0.716	-0.012	0.994	0.1-32	0.700	-0.012	0.994	0.1-32
o-Anisidine	0.323	-0.008	0.986	0.1-35	0.310	-0.008	0.985	0.1-35
4-Chloroaniline	0.364	-0.007	0.980	0.1-28	0.358	-0.007	0.978	0.1-28
Dibutyl phthalate	1.024	0.036	0.999	0.1-40	0.916	0.038	0.999	0.1-40
Di-2-ethylhexyl-phthalate	0.279	0.006	0.992	0.1-26	0.283	0.005	0.990	0.1-26

These calibration factors were used to quantify amounts of these compounds in chromatograms obtained from analysis of 13 further tubes which had either been spiked with the internal standard (control tube), the standard carcinogen mixture and the internal standard, or else contained the re-collected split effluent from a previous analysis of a standard tube or a tube used in an emissions test (see Section 6.3.2.5). Using both ChemStation and TargetView, seven of these compounds were observed from the seven tubes which had been spiked with the standard mixture. Amounts found and relative standard deviations were very similar for both processing methods (Table 7-6). For the remaining four compounds a wider concentration range was found due to their presence in control or re-collected tubes. In each case they were found in the same chromatograms using both ChemStation and TargetView.

Table 7-6 Amounts of compounds found from analysis using TOF system of spiked tubes with processing using ChemStation and TargetView

Compound	Amount on tube (ng)					
	ChemStation			TargetView (v2.0)		
	Mean	%RSD	n	Mean	%RSD	n
Acrylonitrile	1.1	4.7	7	1.2	4.3	7
Trichloroethylene	2.5	3.3	7	2.6	3.8	7
1,3-Dichloropropan-2-ol	2.4	5.9	7	2.5	6.2	7
Benzyl chloride	2.3	3.7	7	2.4	3.7	7
o-Toluidine	1.6	2.1	7	1.7	1.6	7
o-Anisidine	1.7	2.4	7	1.8	2.6	7
4-Chloroaniline	1.7	3.5	7	1.7	3.1	7

Correlations between the quantitative data for these compounds given by the two methods are shown in Figure 7-10. Good results were obtained with gradients between 0.96 and 1.12 and $r^2 \geq 0.998$).

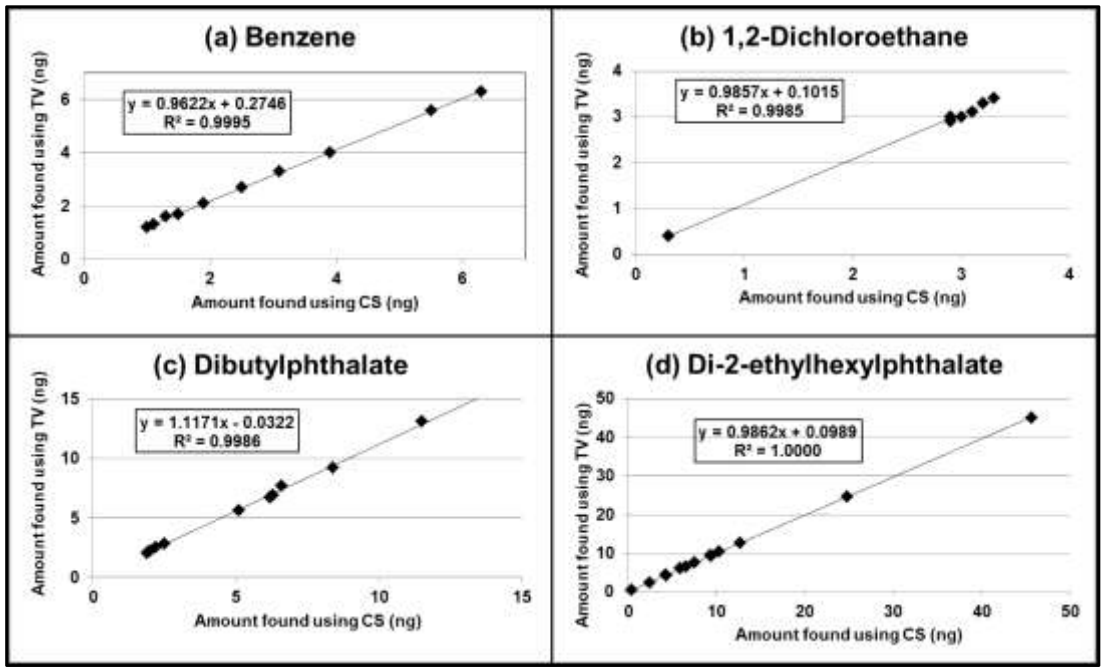

Figure 7-10 Amounts of four VOCs found from analysis of standard and control tubes using the TOF system with ChemStation (CS) and TargetView (TV) processing

These findings therefore show that use of TargetView Plus to process data obtained using the TOF MS can give comparable quantitative data to that obtained using ChemStation, at least for the compounds investigated in fairly 'clean' chromatograms.

7.3.4 Comparison with previous studies

TargetView is a newly developed product and therefore few published studies using the software have been identified by a search of the literature. An investigation by Leppert et al. (2012) used the package to determine chemical warfare agents (CWAs) and their simulants in air. They were able to detect five simulant compounds to a low level using the software and to produce good calibration data for these compounds. No comparison of the performance of the software with that of ChemStation software for compound calibration was undertaken as part of the previous study however.

The study by Leppert et al. (2012) has, in common with the present study, investigated the influence of different matrices on the performance of the software. Their method used fast GC, which results in a faster run time, but more overlapping and co-eluting peaks. Tests of CWAs in gasoline and diesel were also undertaken. Both the present project and this previous study have found the deconvolution process to successfully resolve the peaks of interest from background contaminants.

Another software package available for identifying compounds present in a chromatogram is AMDIS (Automated Mass Spectral Deconvolution and Identification System) which is available through the National Institute of Standards and Technology (NIST). Maddalena et al. (2012) applied this to the identification of VOCs found in the air of newly built Californian homes. The package was used in parallel with ChemStation and resulted in dramatically reduced analysis time and quantitation of compounds that would otherwise not be resolvable in complex mixtures. The automated results however still needed to be reviewed by an experienced analyst. A distinction between the two packages therefore appears to be that, use of TargetView, if the findings so far are replicated with a wider range of chromatograms, could replace the need for processing within ChemStation, which would be give a more straightforward process.

7.4 Conclusions

The tests undertaken in support of this objective have provided confidence in the ability of TargetView compound identification software to identify and quantify target analytes present in material emissions chromatograms. Initial tests focussed on chromatograms containing standard mixtures, followed by examination of chromatograms obtained from a range of emissions tests. Refinement of the settings and development of the software were found to reduce the number of errors associated with the use of this product. For one case of discrepancy between amounts obtained using TargetView and those from use of the ChemStation data analysis package, the possibility existed that ChemStation was overestimating the amount as a result of a closely eluting compound having common ions in its spectrum to that of the target analyte. While most tests have been undertaken using data generated by an Agilent MSD, one set of files from the ALMSCO BenchTOF-dx has also shown promising results. In order to confirm these findings further tests are required looking at different target analytes within a variety of complex chromatograms. If good results continue to be achieved the software could become a useful tool in the processing of data from material emissions tests.

Aspects of this work were presented at three conferences as follows: qualitative work (Indoor Air 2011 conference, Austin, Texas), TargetView processing of door and window samples (Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 2012, Cranfield) and TargetView processing of wall covering materials (Healthy Building 2012 conference, Brisbane, Australia). Details of the papers, which were published in the proceedings of these conferences, can be found in Appendix G.

8 OVERALL CONCLUSIONS

This project has successfully applied the latest generation of thermal desorption instrumentation to the development of improved methods for the characterisation of organic chemicals emitted into indoor air by building and furnishing products. The development of an optimised analytical method and establishment of a quality control procedure provided confidence in the results of analyses undertaken in pursuit of the objectives of the project. The participation in two inter-laboratory comparison exercises during the course of the project has also allowed the accuracy of results obtained to be checked against those of other laboratories.

The first aim of this work was to investigate the application of two screening methods for testing emissions from materials. The Nalophan bag method was found to provide some useful qualitative information about emissions, while the dynamic nature of the process using a micro-scale chamber method (Markes µ-CTE) mirrors more closely that of a larger scale emissions test. The use of a slightly elevated temperature to accelerate the test was found to enhance the emissions without significant distortion of the profile, showing the method to have the potential to be a cost effective and relatively quick method of characterising products with results being obtained within a day. For prediction of the emissions occurring from longer term reference tests of material emissions, the studies undertaken showed that the test temperature and equilibration time would need to be optimised for each material.

The second area of study involved the sorbents used to sample the compounds emitted from materials. It has been successfully demonstrated that use of a multi-sorbent tube, which has the potential to widen the range of compounds that can be determined in a single analysis, in place of the standard Tenax TA tube, does not adversely affect the recovery of compounds classified as volatile organic compounds (VOCs). Investigation of storage performance for nine VOCs on both types of tubes showed that a recovery of within about 10 % of the amount loaded can be expected for both tube types after four weeks storage. Refrigeration of the samplers during storage was found not to be necessary for these compounds over this storage period.

Application of the multi-sorbent tube (containing quartz wool/Tenax TA/Carbograph 5TD) to the determination of very volatile organic compounds (VVOCs) in material emissions demonstrated a significant extension to the number of compounds which can be quantified compared to use of Tenax TA alone. Six VVOCs which appear on at least one target list of chemicals used by national and international schemes for assessing material emissions could be determined up to a sample volume of at least 10 litres. This compares with maximum safe sample volumes for these compounds using Tenax TA alone of between <200 ml and 3.5 litres. 11 other VVOCs emitted from materials and/or also occurring on one or more target list showed more modest improvements in the maximum safe sampling volume possible. This work therefore demonstrates significant progress towards the goal of having a single analysis for the determination of all chemicals of interest. Use of the multi-sorbent tube would result in a significant saving in cost over the requirement for sampling using separate sorbents for the different volatility ranges of compounds. It would also result in more accurate results being obtained for compounds at the more volatile end of the VOC range, for example n-hexane, which are currently determined using Tenax TA alone.

The use of Nalophan bags has been found to be a convenient and economical means of generation of an atmosphere of different mixtures of VVOCs for comparing the performance of different sorbent types for several compounds simultaneously. For semi-volatile organic compounds (SVOCs) the advantage of use of the μ-CTE with an elevated temperature to allow a faster comparison of sorbents was demonstrated, though no improvement in performance from use of the multi-sorbent was identified for the particular compound selected for study.

A further aspect of the development of methods based on thermal desorption for the determination of compounds emitted from materials was its application to the measurement of formaldehyde. This project has confirmed the potential of 2-hydroxymethylpiperidine to act as a derivatising agent for the quantitative determination of formaldehyde in air by thermal desorption. A repeatability of 10 % was obtained using a technique in which filters impregnated with the reagent were inserted into gauze caps and fitted to the front of sorbent tubes during sampling. Successful development of this method would therefore remove the need for separate

analytical instrumentation (typically HPLC) currently required for the determination of this compound. Tenax TA was found to be a suitable sorbent to use with this method, though, as a result of reaction of the reagent with other compounds and the presence in the chromatogram of excess reagent, it would not be possible to determine other compounds using this sampler at the same time.

A range of parameters have been investigated using the time-of-flight (TOF) mass spectrometer (ALMSCO BenchTOF-dx). It has been shown to have significant potential for enhancement in sensitivity over that of a standard quadrupole mass spectrometer. This would be of benefit for toxic and odorous compounds including carcinogens, which there is a need to determine at a low level in material emissions. The use of two analyses at different sensitivity levels, to allow determination of an increased concentration range of compounds from one air sample, has been demonstrated. Good results were obtained for the majority of compounds, but currently this method does not appear to be appropriate for benzene and for the two phthalates studied.

Finally the use of new compound identification software (ALMSCO TargetView) for processing of data generated during emissions tests was explored. Data obtained on systems incorporating both an Agilent MSD and the ALMSCO BenchTOF-dx were investigated. Using the latest version of TargetView, good correlation was achieved, for both systems, between amounts of target compounds found using this software and amounts found using the standard means of manual processing within ChemStation data analysis software. The results obtained therefore demonstrate the possibility of automating the procedure for processing of material emissions data with a resulting reduction in costs.

In summary, this project has demonstrated potential improvements which could be applied to a number of aspects of the testing emissions of organic chemicals from building and furnishing products; in particular in the use of screening tests, the volatility and concentration ranges of compounds detected and in the potential automation of the data obtained.

9 RECOMMENDATIONS FOR FURTHER WORK

9.1 Development of screening tests

This work using the μ-CTE at slightly elevated temperature in comparison with the FLEC has shown the suitability of this approach for some wall covering and flooring materials. Further work is needed to assess the applicability for other products. It is recommended that a temperature of 40 °C and an equilibration time of 2 hours are employed as initial test conditions.

9.2 Selection of sorbents

For the determination of VVOCs, further work could test different sorbent combinations in order to determine the limits possible with current sorbents. Likewise for SVOCs, tests with further compounds are required in order to define the limits possible using current TD technology.

Further work could make use of reference materials which are being developed for material emissions. This would avoid the homogeneity issues encountered from use of samples of building and furnishing materials. For SVOCs the use of moderate heating is recommended to reduce test times. For comparison of sorbent performance for VVOCs, the bag sampling method could be developed to provide standard atmospheres with more controlled concentration, for example, through use of bags fitted with septa for introduction of the compounds of interest. An alternative would be to use a tube loading rig such as that which was used in the stability test of check standard VOCs and is used for loading of tubes for HSL's material emissions proficiency testing scheme. This allows up to 30 tubes to be exposed to a controlled atmosphere of a mixture of compounds at one time.

9.3 Further development of TD based method for determination of formaldehyde

To continue the improvement of this method there is a need to clarify the sensitivity, the range of effective flow rates, the blank levels and to check for possible interferents and stability on storage. There is potential to extend the scope to sampling of indoor air,

which would require determination of robustness to temperature and humidity conditions in the field.

The benefit of using the method based on the reagent 2-hydroxymethylpiperidine (2-HMP) in combination with a reference method (the acetylacetone method) should be built upon by aligning the sensitivities of the two methods. A source of formaldehyde (from a permeation tube or the reference material which is under development) could be used to provide different concentrations at which to test the method.

9.4 Application of TOF MS

With the TOF MS development of methods that fully utilise its potential for detection of carcinogens are required. To achieve this, further tests could be carried out using a range of complex chromatograms, making use of the high/low sensitivity method.

Another possibility is to take advantage of the greater number of data points collected by the TOF MS with the application of fast GC and automation of data analysis to the testing of emissions from materials. In the longer term, if successful, standard methods could be developed (through ISO/CEN) incorporating these benefits.

9.5 Use of TargetView

Further tests are required to demonstrate the application of TargetView to the different emission target lists. In particular, its performance for the determination of trace level toxic or odorous compounds, such as carcinogens, in complex emission profiles needs further assessment. This would involve quantification of compounds appearing on particular lists of target analytes within a variety of chromatograms obtained using both standard quadrupole and TOF MS instrumentation.

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Appendix A Standard operating procedures developed during the project

A.1 Sampling of VOCs emitted from materials using the Micro-chamber/Thermal Extractor (µ-CTE)

A.1.1 Aim

This method describes a screening method for vapour phase organic compounds (volatiles and semi-volatiles) released from materials under simulated real use conditions using the Markes International Micro-chamber/Thermal Extractor (µ-CTE™). This standard operating procedure (SOP) is based upon the sampling method contained within ISO 12219-3:2012 for the "determination of the emissions of VOCs from car trim components – Part 3: Micro-scale chamber method".

A.1.2 Materials and equipment

1) Steel sorption tubes containing Tenax TA or other sorbent(s), sealed with two-piece brass Swagelok caps with single PTFE ferrules on both ends

2) Supply of zero grade compressed air

3) µ-CTE and a range of sample spacers for surface emissions testing

4) Electronic flow meter (an Agilent ADM 2000 has been found to be suitable)

5) Stop watch

6) Tools for cutting material samples.

A.1.3 Related documents

1) Markes International Micro-Chamber/Thermal Extractor (µ-CTE) Operators' Manual, version 3.2, 2009, Markes International Ltd., Llantrisant, RCT.

2) BS ISO 12219-3:2012 "Indoor air of road vehicles – Screening method for the determination of the emissions of VOCs from car trim components – Part 3: Micro-scale chamber method".

A.1.4 Preparation of test specimens

1) The µ-CTE should be pre-heated to the temperature required for the test and the zero air supply turned on at the regulator (and if necessary at the tap on the wall). With the air supply connected to the high flow inlet at the rear of the instrument, the pressure should be set to 12 psi, to give a flow rate of approximately 50 ml min^{-1}. A 'flow check' sampling tube should be connected to the outlet port of one of the chambers and the flow rate checked at the outlet of the tube using an electronic flow meter.

2) The test specimens should be removed from storage and unpacked. If surface emissions testing is appropriate, discs of diameter 45 mm should be prepared with a minimum of delay and placed in the µ-CTE chambers using the required number of spacers to raise the top surface of the material to the top edge of the chamber. If it is appropriate to measure emissions from the bulk material, e.g. polymer beads, adhesives or insulation fibres, representative samples should be placed directly into the chambers (or, if likely to contaminate the chamber, first placed into an inert container).

3) Once the samples are prepared the chambers should immediately be placed into the µ-CTE and the lids to the chambers closed.

A.1.5 Test method

1) After the time required for equilibration, typically 20 minutes to 2 hours, conditioned sorbent tubes are connected to each outlet port and the tube numbers recorded. Measure the flow rate at the outlet of each tube using an electronic flow meter (average of three readings).

2) After 15 minutes remove and cap the sorbent tubes. If required a second set of tubes can be used to sample from the chambers.

3) When the required sampling periods have been completed switch off the power and air to the instrument. Once cool, remove samples from the µ-CTE. Sampled tubes are stored in a plastic box until their analysis using TD/GC/MS (see Appendix A.5).

4) To clean the whole instrument, heat it, including the chambers, at 120 °C for 1 hour with a fast flow of air (30 psi will give about 200 ml min^{-1}). It may also be necessary to clean the chambers further, in which case they should be removed from the µ-CTE, the O-rings removed and the chambers, and any spacers used, heated in a laboratory oven at 150 °C for 2 hours. After cleaning, the µ-CTE should be set at the temperature required for sampling and a set of control samples taken using conditioned sampling tubes.

A.1.6 Calculation of vapour concentrations and specific emission rates

Results should be expressed as area specific emission rates (SERa), with the units µg m^{-2} h^{-1}. The masses of individual vapours or total VOCs determined during analysis can be used to calculate SERa directly, taking into account any amounts of VOCs found on the blank tubes:

$$SERa = \frac{analyte\ mass\ (\mu g)}{Area\ of\ sample\ \ m^2\ \ x\ duration\ of\ vapour\ sampling\ (h)} \quad \textbf{A-1}$$

For the µ-CTE, the duration of sampling is 15 minutes (0.25 hours) and the exposed area of sample is 1.28 x 10^{-3} m^2, so that the equation becomes:
SERa = analyte mass / 3.2 x 10^{-4} (units: µg m^{-2} h^{-1}).

A.2 Sampling of VOCs from materials using Nalophan bags

A.2.1 Aim

This method describes a screening method for vapour phase organic compounds (volatiles and semi-volatiles) released from materials using Nalophan sampling bags. This standard operating procedure (SOP) is based upon the sampling method contained within ISO 12219-2:2012 for the "determination of the emissions of VOCs from vehicle interior parts and materials – Part 2: Bag method".

A.2.2 Materials and equipment

1) Steel sorption tubes containing Tenax TA or other sorbent(s), sealed with two-piece brass Swagelok caps with single PTFE ferrules on both ends

2) Supply of zero grade compressed air

3) Rolls of Nalophan sheeting

4) Cable ties and cable tie tensioning tool/cutter

5) Polyethylene tubing

6) ¼ inch Swagelok fittings

7) In-line flow calibrator (a TSI 4100 Series has been found to be suitable)

8) Thermostatic incubator (an Orbital 5150 has been found to be suitable for temperatures up to 60 °C)

9) Air sampling pumps, TSI SidePak SP130 pumps have been found to be suitable

10) Stop watch

11) Tools for cutting material samples.

A.2.3 Related document

BS ISO 12219-2:2012 "Indoor air of road vehicles – Screening method for the determination of the emissions of VOCs from vehicle interior parts and materials – Part 2: Bag method".

A.2.4 Preparation of bags and test specimens

1) Two 55 cm lengths of the 21 cm wide Nalophan sheeting are cut from the roll. One end of each bag is sealed by fan-folding the material, turning over approximately a 1 cm length and securing using a cable tie.

2) A 10 cm by 10 cm sample of the material to be tested is prepared and placed inside one of the bags.

3) The second end of each bag is sealed around an approximately 10 cm length of ¼ inch wide polyethylene tubing using a pair of cable ties. The end of the tubing outside each bag is fitted with a ¼ inch stainless steel nut and cap for filling and evacuating the bag.

4) Using an in-line flow calibrator each bag in turn is filled with zero grade air at a flow rate of approximately 2 litre min^{-1}.

5) A sorbent tube containing charcoal (to protect the sampling pump from possible contamination) is attached to an air sampling pump set at flow rate of 1 litre min^{-1}. The end cap is removed from one of the bags and using a ¼ inch union the bag fitting is connected to the other end of the tube. Each bag is then in turn emptied of air.

6) The bags are refilled, with the flow rate and time of filling being recorded. The volumes should be approximately 5 litres.

A.2.5 Test method

1) The incubator is equilibrated at the temperature of the experiment.

2) The bags are placed in the incubator with the polyethylene tubing and the Swagelok end fittings protruding from the holes in the side of the incubator wall.

3) At the end of the two hour heating period the end caps on the bag fittings are replaced with ¼ inch unions which are each connected to a conditioned sorbent tube attached to an air sampling pump. Air is drawn through each pump at 100 ml min^{-1} for 10 minutes after which time the pumps are stopped and the tubes are removed and sealed.

4) Sampled tubes are stored in a plastic box until their analysis using TD/GC/MS (see Appendix A.5). A blank tube is included with each batch of analysis.

5) Additional collection of VOCs may be performed as required.

A.2.6 Calculation of sampling bag values

The sampling bag value of a gas component diffused from a test sample is determined as follows:

$$W = Cs - Cb \; x \, Vs \qquad \textbf{A-2}$$

where: Cs is test concentration (µg m^{-3}) obtained under heating at a specified temperature for a specified period of time; Cb is blank concentration (µg m^{-3}) of the sampling bag which was heated without any test sample under the same heating condition; Vs is amount of gas filled in the sampling bag (m^3); W is sampling bag value (µg).

A.3 Sampling of VOCs emitted from materials using the FLEC

A.3.1 Aim

This standard operating procedure (SOP) describes a screening method for vapour phase organic compounds (volatiles and semi-volatiles) released from materials under simulated real use conditions using the Chematec Field and Laboratory Emission cell (FLEC). This SOP is based upon ISO 16000-10:2006 "Determination of the emission of VOCs from building products and furnishing – Emission test cell method".

A.3.2 Materials and equipment

1) FLEC

2) FLEC air control unit (FL-1000)

3) Airtight sample holder (for materials with an irregular surface or large permeability, the carpet test plate, with adaptor if necessary, is suitable for those up to 10 mm depth)

4) Supply of compressed dry and clean air

5) Supply of pure water (that supplied by the Millipore Direct Q has been found to be suitable)

6) Steel sorption tubes containing Tenax TA or other sorbent(s), sealed with two-piece brass Swagelok caps with single PTFE ferrules on both ends

7) CapLok tool/spanners

8) Electronic flow meter (both a TSI 4100 Series in-line flow calibrator and an Agilent ADM 2000 have been found to be suitable)

9) Temperature logger (a Gemini Tinytag View 2 has been found to be suitable. Periodic calibration of the humidity of air supplied by the air control unit also requires a humidity monitor which the View 2 incorporates)

10) Stop watch (or can use pump logging facility)

11) Air sampling pump(s) (TSI SidePak SP130 pumps have been found to be suitable, but require careful setting up to find a position which does not result in flow block errors, a Casella TUFF Plus Personal Air Sampler, fitted with a low-flow adaptor, has been found to be suitable. In this case use of an in-line flow calibrator is recommended)

12) Tube spacer for attaching tubes to FLEC

13) Aluminium foil

14) Tools for cutting material samples

15) Glass desiccator (for periodic checking humidity supplied by air control unit)

16) FLEC Recovery test kit

17) Four-figure balance.

A.3.3 Related documents

1) FLEC Users Guide, Markes International, QUI-1035, Version 1.0, February 2007.

2) FL-1000, FLEC Air Control Instruction Manual, Chematec, Version 1.1, July 1999.

3) "Using the FLEC to determine volatile organic emissions from indoor materials and products", Thermal Desorption Technical Support Note 55, Markes International Ltd., Llantrisant, RCT, August 2009.

4) BS ISO 16000-10:2006 "Determination of the emission of VOCs from building products and furnishing – Emission test cell method".

A.3.4 Preparation of FLEC

1) Remove the humidifier bottle from its clamp and unscrew it. Pour in 400 ml pure water and reseal the bottle and replace it in its clamp. The compressed air supply is then turned on at the tap on the bench. The pressure regulator is pulled forwards and turned gradually clockwise until it reaches a pressure of 2 bar. The knob should be pushed in to lock it in position.

2) The flow controllers on the dry and humid air supplies are set to the required flow (typically 125 ml min^{-1} each). ISO 16000-10:2006 requires a relative humidity of 50 ±5 %RH which is achieved by setting the dry and humid flow controllers to the same value. The combined air flow, which is typically 250 ml min^{-1}, should be checked at the combined air control outlet.

3) Place the FLEC on the test plate or on a clean planar surface. The air flow exiting the FLEC should be checked and should not differ from the inlet air flow by more than 5 %. If it exceeds this difference, check for leaks in the tubing.

4) Allow at least 15 minutes with air flowing through the FLEC for the system to be flushed.

5) Check that one or two sampling pump(s) are charged and set to the required flow, typically 100 ml min^{-1}, using a low-flow adaptor if required. The combined flow through the tubes should not exceed 80 % of the total air inlet flow to the FLEC. Do not turn on the pump(s) yet.

6) Uncap one or two conditioned sorbent tube(s) and attach the non-grooved end to an air sampling pump. Check that the vent cap/tube spacer is inserted into the FLEC vent

air outlet and insert the grooved end of each tube into the FLEC air outlets until they touch the tube spacer.

7) Tighten the tube connections until they are finger-tight. Remove the vent cap then tighten the tube connections with a spanner to make them leak tight.

8) Turn on the pumps and start the stopwatch (or else use the pump logging facility).

8) At the end of the sampling period, turn off the pump(s), loose the connections and disconnect the sorbent tubes. Re-cap the tubes and tighten using the CapLok tool.

A.3.5 Preparation of test specimen

1) The test specimen should be removed from storage and unpacked. If the material is flat and is expected to seal onto the FLEC, a piece of diameter ≥ 200 mm is cut. If the material is not expected to seal onto the FLEC, due to having a large permeability or irregular surface, a circular sample is cut which will sit inside the test plate (150 mm diameter). This plate can accommodate samples up to 10 mm in depth. Very thin samples can be cut to a diameter of 170 mm and sit inside the FLEC supported on a clean planar material (e.g. piece of clean aluminium foil, glass or stainless steel) of diameter greater than that of the FLEC.

2) The material sample is placed under the FLEC and this is taken as time 0 hours.

3) Set up temperature logger to log the temperature for the duration of the experiment and start it logging. (Note that ISO 16000-6:2011 requires the test to be undertaken at 23 ±2 °C).

4) Check that the air outlet flow has not been reduced as a result of adding the sample. If it differs by more than 5 % from the air inlet flow then the sample needs to be placed in an airtight sample holder.

A.3.6 Test method

1) Take air samples from the FLEC air outlet using conditioned sorbent tubes.

2) The ISO 16000-6:2011 standard specifies that duplicate samples should be taken at 72 (±2) hours and 28 (±2) days after the start of the test. Additional samples can be taken as required.

3) The material may be removed from the FLEC between the 3 and 28 day sampling if required, but should be stored in a location which allows a flow of air and does not allow contamination from other stored specimens. (ISO 16000-6:2011 requires the material to be stored at 23 ±2 °C and at 50 ±5 %RH). The material should be returned to the FLEC at least 24 hours before the 28 day sampling.

A.3.7 Cleaning of the FLEC

The FLEC is cleaned by removing all fittings and the sealing O-ring and washing the inner surface with a diluted alkaline detergent, followed by rinsing with purified water. The inner surface is then rinsed with 2-propanol after which it is heated in an oven at a temperature of 100 °C for 2 hours.

A.3.8 Recovery test

1) A volume of n-dodecane (or other chemical of interest) is placed in the 2 ml ground glass vial included with the recovery test kit and this is weighed on a 4-figure balance. The vial is then fitted into the ground glass plate which is placed on the insulating cushion. The FLEC is placed centrally onto the glass plate with the inlet air flow applied.

2) Air sampling is undertaken from the FLEC air outlet after allowing time for equilibration (ISO 16000-10:2006 specifies 24 hours from the start of the test).

3) On removal of the vial from under the FLEC it is re-weighed and this value is used to calculate the expected average vapour concentration in the cell. Recovery is obtained from a comparison of the measured and expected vapour concentrations.

A.3.9 Periodic humidity check

A humidity monitor should be placed inside a glass desiccator of appropriate diameter for the FLEC to seal onto. With the FLEC set up with air flowing through it should be placed onto the desiccator. After 30 minutes equilibration the relative humidity within the desiccator should be recorded. To satisfy ISO16000-10:2006 a value of 50 ± 5%RH should be obtained. If the value falls outside the range check the flow path for leaks.

A.3.10 Calculation of vapour concentrations and specific emission rates

Results should be expressed as area specific emission rates (SERa), with the units $\mu g\ m^{-2}\ h^{-1}$. The masses of individual vapours or total VOCs determined during analysis can be used to calculate SERa directly, taking into account any amounts of VOCs found on the blank tubes. The mass of x (µg) emitted by the exposed area of the material during the emissions test (Mx) is the mean of the masses found on the duplicate samples taking into account the fraction of the air flowing through the FLEC which is sampled onto the tubes.

$Mx = Cx$ (i.e. mean of M_1/V_1 and M_2/V_2) x V

where Cx is the concentration of vapour in the emission cell (in $\mu g\ ml^{-1}$)

M_1 and M_2 are the mass of VOC retained by the duplicate tubes (in µg)

V_1 and V_2 are the volumes of air pumped through each tube (in ml)

and V is the volume of air passed into the cell during the emission test (in ml)

To derive the mass of x (µg) emitted by the exposed area of sample per hour, multiply Mx by 60 and divide by the actual duration of the test in minutes: = Mx x (60/T)

To derive the area specific emission rate, at time t, in µg m^{-2} h^{-1}, multiply the result from the above equation by 10,000 (cm^2) and divide by the exposed sample surface area (= 177 cm^2).

$$SERa = Mx \times (60/T) \times 10{,}000/177 \qquad \textbf{A-3}$$

A.4 Conditioning of tubes using the TC-20

A.4.1 Scope

This standard operating procedure (SOP) describes the conditioning of sorbent tubes using the Markes International tube conditioning rig (TC-20™). Conditioning of tubes is required before their use for air sampling/emissions testing.

A.4.2 General

1) The TC-20 has a temperature range of 50 to 400 °C and a timer range of 1 minute to 99.59 hours at flow rates in excess of 50 to 100 ml min^{-1}.

2) A checklist listing important points to remember from the procedure appears on the last page of this SOP.

A.4.3 Related document

TC-20 Sample tube conditioning/dry-purging rig, Operators' Manual, version 6.2, Markes International Ltd., Llantrisant, RCT, July 2009.

A.4.4 To note before using

1) Do not block or cover the rear of the unit and allow at least 200 mm of clear space to the rear of the instrument. Note that the TC-20 emits approximately 250 watts of heat when set at 400 °C.

2) On reaching the end of the run time, keep the fan running, i.e. keep the TC-20 switched on, until it has cooled to below 100 °C.

A.4.5 Operation of the TC-20

1) If necessary disconnect the manifold assembly from the TC-20 using the quick release union and place the assembly in a convenient position to insert tubes.

2) Push the non-grooved end of the sorbent tubes to be conditioned into the manifold block such that the sampling ends (grooved ends) are away from the manifold. Any number of the 20 tube positions may be left empty if required (but it is most efficient to condition tubes in batches of 20 as gas will be used anyway).

3) Using the handle guide the assembly down into the heater block, if there is any resistance do not force the block down. Connect the manifold assembly to the TC-20 using the quick release union.

4) Turn on the power to the TC-20 (switch on rear of instrument).

5) Turn on the carrier gas (high purity helium or nitrogen) to the unit and, if necessary, adjust to ~24 psi on the regulator (Gas03) (to give a pressure of 20 psi on the dial at the front of the instrument). This gives a flow rate of approximately 60 ml min^{-1} through each tube. Table A-1 gives a list of approximate flow rates at various pressures.

6) If necessary, set the temperature for the conditioning programme. 320 °C is used for tubes packed with Tenax TA and for those packed with quartz wool/Tenax TA/Carbograph 5TD (MS1) and with quartz wool/Tenax TA/Carbopack X (MS2). On the upper digital display press and release **P. '**SP1' should be displayed flashing on the top line of the display. Use the Up and Down arrows to set the required temperature. When 320 °C is displayed press and release **P**. (Note that different conditions apply for freshly packed tubes – follow the suppliers' recommendations).

7) If necessary set the required time for the conditioning programme. The standard cycle time is 45 minutes and may be set from the instrument's last use. On the lower digital display press and release **P**. Use the Up and Down arrows to select the required time. Press and release **U** for display to revert to the normal running mode.

8) Having allowed 5 minutes from the time the gas is flowing through the tubes (so that the charcoal trap is flushed); press the **U** button on the lower digital display to start the programme. Check that the instrument starts to heat up and the time to increment. Use a stop watch to remind you when the run will have finished.

9) Complete TC-20 record book and log the conditioning in the appropriate tube record book.

10) When the set time is complete, as shown by the timer reaching the set time, leave the carrier gas flowing, but at the Gas03 reduce the pressure until it reads 5 psi on the front of the instrument. At the same time remove the manifold assembly and place it on the cooling plate leaving the quick release union connected so that gas continues to flow through the tubes.

11) When the tubes have cooled sufficiently to be comfortably handled, turn off the carrier gas, disconnect the gas supply quick release union and place the manifold assembly in a suitable position for removing the tubes (it is also possible to remove the tubes with the manifold still connected to the instrument).

12) Pull steadily to remove the tubes from the manifold assembly and cap tubes promptly. It is best to tighten caps to finger tight initially then when they have all been capped go back and tighten each using the cap-lock tool.

13) If wishing to condition a second batch of tubes, ensure that the temperature of the heated block is below 100 °C before loading further tubes.

14) Once tubes have all been removed from the manifold, ensure that the manifold is disconnected from the gas supply and turn off gas supply at the Gas 03 and, if the spiking rig is not being used, also at the gas tap.

15) When finished conditioning and the temperature of the heated block has cooled to below 100 °C, turn off the power to the TC-20.

Table A-1 Pressure applied to TC-20 and resulting flow through each tube

Pressure (psi)	**Flow rate (ml min^{-1})**
10	30
15	45
20	60
25	75
30	90

A.4.6 Important points to remember when using TC20 for conditioning

1) Check that time and temperature are correct, re-set if necessary

2) Load tubes correct way round (un-grooved end into manifold)

3) Turn on carrier gas at correct pressure (20 psi on the instrument)

4) Allow 5 minutes for helium to purge through the charcoal trap

5) Start conditioner and set stop-watch

6) When programme complete raise tubes and reduce pressure to 5 psi

7) When cool remove tubes and turn off gas

8) Ensure block temperature is <100 °C before further conditioning

9) Do not turn off heater block power until it is below 100 °C.

A.5 Determination of VOCs trapped on adsorbent tubes containing Tenax TA (or multi-sorbents including Tenax TA) using TD/GC/MSD system

A.5.1 Aim

This method describes the determination of a target list of volatile organic compounds (VOCs) which have been trapped onto adsorbent tubes containing either Tenax TA or similar sorbents during sampling of ambient, indoor or test chamber air and are analysed by thermal desorption and gas chromatography/ mass spectrometry. Other sorbents which have been investigated are MS1 (quartz wool/Tenax TA/Carbograph 5TD) and MS2 (quartz wool/ Tenax TA/Carbopack X). This standard operating procedure (SOP) is in accordance with the analytical method required by ISO16000-6:2011 for active sampling of indoor and test chamber air.

When used with an appropriate sampling volume (for active samples) or exposure period (for diffusive samples) the method is optimal for the measurement of non-polar and slightly polar VOCs within the volatility range of n-hexane to n-hexadecane. Some very volatile compounds (VVOCs) and semi-volatile organic compounds (SVOCs) can also be analysed that are outside this volatility range. The total amount of VOCs present in the air is represented by the 'TVOC' value which is obtained by summing all compounds eluting between n-hexane and n-hexadecane and quantifying as toluene equivalents.

A.5.2 Materials and equipment

1) Steel sorption tubes containing Tenax TA or other sorbent(s), sealed with two-piece brass Swagelok caps with single PTFE ferrules on both ends

2) DiffLok caps for use during analysis of tubes

3) Syringes, 1 µl to 1 ml capacity

4) Volumetric flasks, up to 100 ml capacity

5) Pasteur pipettes, glass, or other means of dispensing liquid

6) Screw top glass vials

7) Balance, four decimal places

8) Methanol, analytical grade, for preparing calibration solution for liquid spiking

9) Organic compounds for calibration (as pure as available)

10) Helium, CP grade, as carrier gas

11) Nitrogen, as TD cold trap purge gas

12) Markes Calibration solution loading rig (CSLR™) connected to supply of helium, CP grade.

A.5.3 Thermal desorption/gas chromatographic/mass spectrometer system:

1) A Markes two-stage thermal desorber (TD-100) fitted with a heated transfer line

2) An Agilent 6890 gas chromatograph (GC) fitted with a capillary column and coupled to a 5973 mass selective detector (MSD). The output from the GC/MSD will be handled using Agilent ChemStation software, running on a suitable computer.

A.5.4 Related documents

1) Agilent GC-MSD ChemStation and Instrument Operation Manual

2) Markes TD-100 Operators' Manual, Version 1.0, Markes International Ltd., Llantrisant, RCT, 2009.

3) ISO Standard 16000-6:2011 "Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID".

A.5.5 Sampling and sample preparation

1) Freshly packed tubes are conditioned thoroughly according to the supplier's recommendations. After this a representative sample of tubes are analysed to check for the presence of any target analyte(s) before use.

2) After analysis the tubes are stored in the area designated storage area for tubes requiring conditioning.

3) Prior to further use, the sorption tubes are conditioned either in the TD-100 or in a tube-conditioning rig (TC-20). If the TD-100 is used the tubes are heated to 320 °C in a helium flow of 50 ml min^{-1} and with a flow path of 200 °C. If a TC-20 is used (Appendix A.4) high purity helium or nitrogen (at between 50 and 100 ml min^{-1}) is passed through the tubes for at least 45 minutes total time with the temperature set at 320 °C.

4) The sample and travelling blank sorption tubes are enclosed in a sealed container after sampling and stored at ambient temperature until analysis if they contain Tenax TA sorbent alone. If the samplers contain multi-sorbents storage in a refrigerator may be preferable, in which case the caps on the tubes must be re-tightened once they have equilibrated at the temperature of the refrigerator.

A.5.6 System checks – every day before operation

1) This procedure assumes that the thermal desorber, gas chromatograph, mass spectrometer and computer are in an operational state i.e. the instruments are connected to the mains electricity, helium carrier gas and nitrogen purge gas and are switched on. If this is not the case refer to the manufacturers' manuals for the initialising procedure.

2) If necessary start the 6890-5973/Enhanced (Agilent GC MS), Enhanced Data Analysis and 'TD-100' control software. Set up the TD/GC/MSD conditions (see Section A.5.9).

3) Open manual tune (Instrument, Edit tune parameters). Click on 'Prof', switch the calibration gas (PFTBA) to open and allow it to stabilise. Monitor 69, 18 and 28 ions as per cent abundance and record on the 'MSD System Performance Check Chart'. If value is outside the normal range for the instrument investigate e.g. test for a leak, check reference gas bottle or tune accordingly.

4) Click on 'Stop' to stop instrument scanning, click on 'MS off' then 'OK'.

5) If system has been idle for several hours (e.g. over a weekend) run at least one empty tube. Check that no peaks for any of the target analytes on the resulting chromatogram exceed the lowest calibration level. If any compounds exceed this level repeat the process.

6) Run a QC standard containing approximately 100 ng of each of 11 compounds (see Section A.5.10 for spiking procedure) and 50 ng of the internal standard (d8-toluene is normally used). This standard should be followed by an empty tube. Enter results into the QC chart and check that the response values fall within ±2 SD (if not run a further standard) and retention times within 0.1 minutes of recent runs (if not re-lock the method). If the criteria are still not met, investigate, e.g. tune MS. Monitor electron multiplier voltage, ion focus voltage and repeller voltage for trends.

A.5.7 Tuning MSD

1) This should be carried out after changing column or if performance deteriorates (see MSD 'Tuning Parameters' sheet for date of last tuning).

2) Click on 'View' 'Tune and vacuum control' then 'Tune' 'Standard Spectra tune'.

3) When tune finished record date, tune type, multiplier voltage and repeller voltage on MSD 'Tuning Parameters' sheet.

4) Click on 'View' 'Instrument control'.

A.5.8 Chromatographic run sequence

1) Spike all the samples (and blanks) to be run with 0.5 µl of the internal standard and purge each at 80 - 100 ml min^{-1} for approximately three minutes.

2) Set out the tubes to be run in the order for loading and change the end caps to analytical caps. Note that Silcosteel® caps are used on the sampling end of the tubes and plain caps on the non-sampling end. A typical run of sorption tubes can consist of tubes expected to have small amounts of analytes (including blanks and tube conditioning checks) then air samples. A maximum of 20 samples are run before running a QC tube.

3) Set up the sorption tube sequence in the TD-100 software: 'File' 'New Sequence' 'Automation' (or alternate mouse button click) 'Add Set of tubes', enter method (in TD-100 folder in program files) and first and last tube. Add further sets if required. Save as 'yymmddn' on c:\MSDChem\1\Data\ current folder, where n = a for the first sequence undertaken in a day and b is the second etc.

4) Click on the tick to make this the controlling sequence (other open sequences can then be closed). Click on '+' and enter the tube numbers (instead of sample01 etc.). Save file. View, options, reporting, create report file (on C:\Msdchem\1\Data\current folder) as yymmddn.csv.

5) Set up the sequence in the ChemStation software: In '6890-5973/Enhanced' software go to 'Sequence'. 'import sequence from csv file' (leave sample names as 1, vial no. as 2, start import at line 5 and end at line 100 in order to import correctly). View sequence verification if desired. Save sequence in current folder as yymmddn.s where n = a for the first sequence undertaken in a day and b is the second etc.

6) 'Edit sequence', Check/set data path as c:\Msdchem\1/Data/current folder and method path as c:/Msdchem/1/methods.

7) Check/change: method, data file name(s) yymmddiehaxxx, comments (add sample description), leave other fields as 1, blank, no update, no update, no update, no update. Click on 'OK' 'save' 'Sequence' 'Run sequence' – ensure that 'full method' is selected and that 'overwrite existing data files' is not checked. Select 'Run sequence'.

8) Load the sorption tubes into the TD-100 tray(s). In the TD-100 control software, check on the status screen that all temperatures and pressures are normal.

9) Start the TD-100 running by clicking 'Instrument' 'Run' (or clicking on the right pointing arrow) and check that the system starts correctly.

10) When the run is complete, remove sorption tubes from the trays, increment letters associated with tube number on the bags for the tubes and update tube log book.

A.5.9 Instrument conditions

TD-100 conditions:

Standard 2 (3) desorption

Split on in standby:	Checked and set at 10 ml min^{-1}
Flow path temperature:	210 °C
Minimum Carrier Pressure:	10 psi
GC Cycle time:	74 min
Cold trap packing:	Materials emission, U-T12ME-2S
No dry purge	
PrePurge time:	1 min at 30 ml min^{-1} (trap not in line, split on)
Tube/Sample desorption	
Tube desorb time:	8 minutes
Tube desorb temperature:	280 °C
Trap flow:	50 ml min^{-1}
Split on:	No
Trap settings	
Pre-trap fire purge:	1 min, trap flow 20 ml min^{-1}, flow 10ml min^{-1}
Trap low:	-10 °C
Trap heating rate:	Max
Trap hold:	3 minutes
Split flow:	10 ml min^{-1}
Trap high:	300 °C

Note that if levels of VOCs are expected to be high a TD method incorporating a higher split flow may be employed.

GC/MS conditions:

Inlet and Injection Parameters:

Sample inlet: GC

Injection Source: External device

Injection location: Front, 'Use MS' checked

No injector or valves configured.

Back inlet Mode: split, gas = He, heater on, set at 200 °C

Front inlet Mode: splitless, gas = He, pressure set at 20.1, total flow set at 5.4

Purge flow to split vent 1 ml min^{-1} @ 999.99 min

Column: a 60 metre DB-5, 0.25 mm I.D., 0.50 micron film column is suitable

Column 1, Constant flow of 1.3 ml min^{-1}

Inlet: front, Detector: MSD, Outlet psi: vacuum

No detectors or signals set-up

Retention time locked to cyclohexanone at 24.61 minutes.

Oven parameters:

Initial temperature:	35 °C
Initial hold:	1 minute
Ramp 1:	2 °C min^{-1} to 75 °C and no isothermal hold
Ramp 2:	5 °C min^{-1} to 140 °C
Ramp 3:	10 °C min^{-1} to 300 °C
Final hold:	12 minute isothermal hold has been found to be suitable (62 min run)

Note: A shorter GC run can be used for the analysis of standards. Once the retention time of the last component to elute has been established the temperature program can be modified to finish a minimum of two minutes after this time.

Aux

Thermal #2 (MSD transfer line):	280 °C
Runtime:	Not set
Options:	Pressure units psi
MS tune file:	stune
MS Scan Parameters	
EM voltage:	0 rel. to tune value
Solvent delay:	0 minutes
Acquisition Mode:	Scan

Scan Parameters:

Scan Range:	20.00 to 450.00 Daltons
Threshold:	100 counts
Sampling rate:	1
Zones	
MS Source temperature:	230 °C
MS Quad temperature:	150 °C

A.5.10 Calibration and quality control

1) Calibration standards are prepared for the target analytes required for the particular application. Place clean, dry stoppered, flasks in balance room. Weigh flasks until mass is steady. Add compound to flask. Replace the stopper and reweigh the flask.

2) Repeat adding the standard materials in turn, weighing the flask between each addition. Make the volumes up to the mark with solvent (methanol is preferred but other solvents such as acetone, ethanol or ethyl acetate may be required to dissolve the less volatile compounds or for stability reasons in which case a solvent delay will be required on the MS). Label the flask with a unique name for the mix and with the make-up date. Separate solutions of d8-toluene are prepared for the internal standard.

3) Dilute the stock standards with the solvent to produce standards covering the appropriate range of analytes on a sorption tube when spiked with 1 µl of solution. It is recommended to prepare two stock solutions one of which contains approximately three times the amounts of each analyte as the other. Ten-fold dilutions of each stock solution will result in a good range of concentrations. The internal standard is diluted so that the appropriate amount is spiked onto the sorption tube from 0.5 µl solution. The standard solutions are stored in a spark-free laboratory refrigerator.

4) The calibration standard masses are as follows:

If e.g. Flask A contains 'a' grams of toluene in 100 ml, then 1 µl contains a*10,000 ng (and in 50 ml 1 µl contains a*20,000 ng). Reduce this figure accordingly to take into consideration any dilutions made and volume spiked. Note: Allowance must be made for purity and isomeric composition, use the appropriate 'VOC calib. solns.' spreadsheet to calculate the masses.

5) Load a sorption tube into a Markes International calibration solution loading rig (CSLR™) and set a flow of between 80 and 100 ml min^{-1} of clean, dry gas (the flow rate is checked by attaching a flow meter to the outlet of the tube). Using a syringe, accurately transfer 0.5 µl of the internal standard, followed by 1 µl from the most dilute standard solution onto the sorption tube, ensuring that the tip of the needle gently touches the gauze and is held in place for 5 seconds. Allow the tube to purge for approximately three minutes. Record the date, the standard level, the syringe used and the spiking order in a laboratory notebook.

6) Repeat previous paragraph making injections in order of increasing concentration until all the required calibration standard sorption tubes have been prepared.

7) Once standards have been run check baselines of target analytes and assignments for each dilution using 'Qedit' (see Section A.5.11).

8) Suitable quality control charts are produced for the compounds present in the QC solution based on in-house produced tubes spiked with this solution. The data is collected over a span of time so that realistic distributions are determined.

A.5.11 Processing of results

1) In 'Data Analysis' software, load a GC/MS run. Check that the correct quantification method is loaded (see header) then do 'quantitate' 'calculate' followed by 'Qedit' to check integration. After this do 'quantitate' 'generate report' (summary, to screen).

2) Select everything in the report test file and, in Excel, paste it into the appropriate 'quantitation translation' conversion sheet at C1. When 'Text import' box comes up, uncheck 'Tab' and check 'Merge delimiters' and 'space'. Copy and paste the results into the relevant results spreadsheet (Note that for the sample information in Column A it is necessary to use 'Paste Special' and import as 'text').

3) For TVOCs and compounds not included in a quantification method use 'integrate' 'integration results' 'copy' 'close', then paste into a spreadsheet.

A.6 Determination of VOCs trapped on adsorbent tubes containing Tenax TA (or multi-sorbents including Tenax TA) using TD/GC/TOF MS system

A.6.1 Aim

This procedure describes the operation of Cranfield Health's Markes/Agilent Thermal desorption/gas chromatography/time of flight mass spectrometry (TD/GC/TOF-MS) system located in Building 52a Room T710 for the determination of a target list of volatile organic compounds (VOCs) which have been trapped onto adsorbent tubes containing either Tenax TA or similar sorbents during sampling of ambient, indoor or test chamber air. Where details are the same as in the parallel procedure using the TD-100/GC/MSD system (Appendix A.5) the appropriate section of that procedure is referred to.

A.6.2 Materials and equipment

As in A.5.2 except that nitrogen is also used for venting the TOF.

A.6.3 Thermal desorption/gas chromatographic/mass spectrometer system

1) A Markes Series 2 UNITY two-stage thermal desorber connected to a Markes Series 2 ULTRA autosampler fitted with a heated transfer line

2) An Agilent 7890 gas chromatograph (GC) fitted with a capillary column

3) An ALMSCO Bench TOF-dx time of flight mass spectrometer

4) Markes UNITY 2 software, ALMSCO ProtoTOF and dx-Connect software and Agilent ChemStation software, running on a suitable computer.

A.6.4 Related documents

1) Agilent MSD ChemStation Software – User Information

2) Markes UNITY Operators' Manual, ULTRA Operators' Manual and UNITY Technical Support manual

3) ALMSCO BenchTOF-dx Operator and Installation Manuals, Version 2.0, March 2010.

A.6.5 Sampling and sample preparation

1) As in A.5.5, except that conditioning is undertaken either using the UNITY or the TC-20.

A.6.6 System checks – every day before operation

1) This procedure assumes that the UNITY, ULTRA, GC, TOF and computer are in an operational state i.e. the instruments are connected to the mains electricity, helium carrier gas and nitrogen purge gas and are switched on. The light on the front of the ULTRA should be greeny/yellow in colour, the GC screen should be illuminated (press 'status' to see if it is ready to run) and the BenchTOF-dx should have green and orange lights lit (open the door on the RHS of the instrument to see these). If this is not the case refer to the manufacturer's manuals for the initialising procedure.

2) The helium should always be on when the instrument is running: check and set if required (Gas01, upper toggle valve and gauge) at about 55 psi (it needs to be 5-10 psi above the highest column pressure). The nitrogen (lower toggle valve and gauge) should be set at 50 psi. **If necessary open the lower toggle valve**.

3) Normally the instrument control software packages should be left running, but, if necessary, start them in the following order: UNITY control software, ProtoTOF, dx-Connect then ChemStation software (separate packages for controlling GC oven and processing data).

4) Check 'Pump and vacuum settings' tab in ProtoTOF 'Settings mass spectrometer/measurements'. Flight tube pressure should be ≤ 6 e-007, motor rotation ~ 1000 Hz, target speed reached = yes, motor power ~ 30, pump temperature = OK, electronics temperature = OK.

5) Check that TOF status is 'safe standby' (bottom right of ProtoTOF screen). Bring it up to operational settings by clicking on 'safe standby on/off' (red/yellow circle on task bar). It will first say 'preparing' then after a few minutes it will become 'ready'. While waiting, look at the 'voltages' tab in 'Settings/mass spectrometer/ measurements' and watch the settings increase to their set points. Most increase very quickly; detector voltage may take a few minutes.

6) Once the TOF has become 'Ready', do an air/water check by selecting 'Tools' 'Air/water check' 'Start' 'Yes'. Record the resulting ratio on the 'TOF System Air Water Check Chart'. **If instrument fails the check investigate, if it passes continue.**

7) One place to check for leaks is the GC-TOF transfer line. In 'measurement' uncheck 'Start/stop on external trigger'. Press 'Set'. Click on 'Start' to start scanning. Alternate click to see spectrum. Expand scan range to 70-90 (looking for mass 83). Spray air duster around the connection and watch the spectrum – if it goes up tighten one of the two nuts while holding a second spanner against the flats to stop free rotation. Stop scanning when finished and remember to reverse setting in 'measurement'.

A.6.7 Auto signal optimisation and mass calibration

1) This should be carried out after changing column, temperatures, filament voltage or mass range, otherwise about every couple of weeks (see TOF 'Tuning Parameters' sheet for date of last tuning).

2) Carry out a Mass Calibration. 'Tools' 'Mass Calibration' 'start autocalibration', then 'yes'. See BenchTOF-dx Operator manual p.20-21. When it finishes click on 'set as defaults' then yes then 'close'.

3) Check masses for 69, 131, 219 and 502 after mass calibration and repeat mass calibration if necessary. Alternate mouse click to see the spectrum. 'Settings', 'Mass spectra', change mass representation to 0.1 amu.

4) Do an Auto Signal Optimisation (ASO, tune) by selecting 'Tools' 'Automatic Signal optimisation' 'Start' then 'Yes'. The valve containing calibration gas opens (hear a click). If autosignal optimisation is successful it asks you if you wish to accept the new parameters, say 'yes' then 'close'. Note last selected detector voltage from log file in C:\ProtoTOF\AutoOpt and record on 'TOF Tuning Parameters' log.

5) When ASO is complete repeat the Mass Calibration.

A.6.8 Preparing TOF for a run

In ProtoTOF, 'Remote Control' 'Settings mass spectrometer/ measurements' 'Data handling' enter appropriate filename: '<yyyymmdd>ieht'. Add a text description if desired. Note that this is a description for the run and not each sample. Select 'set' then 'start'. At bottom right of screen it should now say 'Wait for trigger'. Data collection will start when TD cold trap fires.

A.6.9 Chromatographic run sequence

1) If system has been idle for several hours (e.g. over a weekend) run a heat trap and/or at least one empty tube (see below for setting up the sequence for the empty tube(s)).

2) For a 'heat trap' check that the appropriate UNITY software and ChemStation methods are loaded and selected then do 'Instrument' 'Heat trap'. When you get the prompt 'Heat trap with controlling method parameters?' say 'yes'. Check that no peaks for any of the target analytes on the resulting chromatogram exceed the lowest calibration level (or a level of significance). If any compounds exceed this level repeat the process.

3) Spike all the samples and blanks to be run with 0.5 µl internal standard and purge each at 80 – 100 ml min^{-1} for approximately three minutes.

4) Set out the tubes to be run in the order for loading and change the end caps to analytical caps. Note that Silcosteel caps are used on the sampling end of the tubes and plain caps on the non-sampling end.

5) Load the sorption tubes into the ULTRA tray(s). Tubes go with the sampling (grooved) ends to the right (note notch in tray to remind you). Tube position 1 is to the back of the tray. Insert tray into ULTRA until it reaches a stop, not further.

6) Select 'UNITY' software. From 'File' 'open' (make sure .mth files are listed and not .seq ones) load the UNITY method as in A.6.10. Click on the tick (on task bar) to make this the controlling method; this causes the UNITY to come up to the baseline temperatures set in the method. It is good practice at this point to close all other open methods.

7) Check split flow is as required by looking at total flow readout on GC front panel. To locate the total flow readout, press 'Back inlet' key on the front of the GC, then use the scrolling keys (up/down arrows) to scroll down to see 'total flow'. In the UNITY method screen, check the 'split on in standby' checkbox. If required use the rear needle valve situated on the top of the UNITY to adjust the flow. A typical value is 25 ml min^{-1} (with trap flow also set to 25 ml min^{-1}). This gives an overall split flow of 32.8:1. (Note that a different set of split flows may be used depending on the levels of VOCs expected). Record the actual split flows in the 'Sample Run' book.

8) Check trap flow is as required by looking at total flow readout on GC front panel. In the UNITY software window, select 'Instrument' then 'Set Gas Flow' and select 'Split on' to 'No'. Adjust the flow as required using the front needle valve situated on top of the UNITY. Record value in 'Samples run' book. Press 'stop' to stop gas flow. Then record flow with split set to 'Yes'. Then stop the instrument again.

9) Set up the sorption tube sequence in the UNITY software: 'File' 'New' 'Sequence' 'Automation' (from menu or alternate mouse button click) 'Add ULTRA set' select (file opens dialog box) required method (in UNITY folder in program files) and first and last tube. Add further sets if required. Save as 'Tyyyymmddn' in current TOF folder (c:\msdchem\1\Data\ Tyyyymmdd - see samples run book for current folder), where n = a for the first sequence undertaken in a day and b is the second etc.

10) Click on the tick (in toolbar) to make this the controlling sequence (other open sequences can then be closed). Click on '+' and enter the tube numbers (instead of sample01 etc.). Save file. View, options, reporting, create report file (in current TOF folder) as Tyyyymmddn.csv), where n = a for the first sequence undertaken in a day and b is the second etc.

11) Set up the sequence in the ChemStation software: In ChemStation software go to 'Sequence', 'Import sequence from csv file' this brings up a dialog box. Check (and set if necessary) that 'sample names' is '1', vial no. is '2', and click on 'OK'. This

produces a second dialog box. Check (and set if necessary) that ‘start import’ is at line 5 and ‘end’ at line 100 ‘OK’. Specify input file format to be ‘.csv’ and select the .csv file created using the UNITY software. View sequence verification if desired (brings up a text window for inspection – useful for large numbers of tubes). Save sequence (Menu ‘Sequence’, ‘Save sequence’) in current TOF folder as Tyyyymmddn.s where n = a for the first sequence undertaken in a day and b is the second etc.

12) ‘Edit sequence’, Set data path as current ChemStation folder (c:\msdchem\1\Data\Cyyyymmdd – see sample run book for current ChemStation folder) and check method path is c:\msdchem\1\methods (top right of window).

13) Check/change: method, data file name(s) ‘<yyyymmdd<ieht<nn>’, comments (add sample description), leave other fields as 1, blank, no update, no update, no update, no update. Click on ‘OK’. ‘Save’ ‘Sequence’ ‘Run sequence’ – ensure that ‘full method’ is selected and that ‘overwrite existing data files’ is not checked. Select ‘Run sequence’.

14) In UNITY control software; check on the status screen (bottom of the page) that all temperatures and pressures are equal to their set points (except UNITY Bobbin Temperature).

15) Check that dx-Connect is running; if not, start it now.

16) Go to ProtoTOF window and check TOF status is still ‘Ready’. If it is not, click ‘Stop’, ‘Set’, ‘Start’. Proceed when status becomes ‘Waiting for trigger’.

17) Start the UNITY running by clicking ‘Instrument’ ‘Run’ (or clicking on the right pointing ‘Play’ arrow) and check that the system starts correctly.

18) When the run is complete, remove sorption tubes from the trays and update tube log book.

A.6.10 Instrument conditions

UNITY conditions:

Standard 2 (3) desorption

Standby ‘Split on’:	Ticked
Flow path temperature:	210 °C
Minimum Carrier Pressure:	10 psi
GC Cycle time:	74 min
Cold trap packing:	Materials emission, U-T12ME-2S
Pre-Desorption	
No dry purge:	(option not fitted)

PrePurge time:	1 min (trap not in line, split on)
Tube/Sample Desorption	
Tube desorb time:	8 minutes
Tube desorb temperature:	280 °C
Split on:	Ticked
Trap Settings	
Pre-trap fire purge:	1 min
Trap low:	-10 °C
Trap heating rate:	Max
Trap high:	300 °C
Trap hold:	3 minutes

GC conditions:

Inlet and Injection Parameters:

Sample inlet: GC, Injection Source: Manual, 'Use MS' not checked, Inlet location: Front

GC Edit Parameters

ALS - No injectors

Inlets - SSL Front – Nothing checked

Inlets – SSL Back, Heater: 200 °C (checked) Pressure: 23.386 psi (checked)

Total flow: greyed out, Septum purge flow: 3 ml min^{-1} (checked), Septum pure flow made: Standard, Gas saver on: not checked

Mode: splitless, purge flow to split vent: 20 ml min^{-1} at 999.99 min

Columns - a 60 metre Agilent DB-5, 0.25 mm I.D., 0.50 micron film column is suitable (entered as 78 m due to restrictor on MS end: 2.5 m of 0.15 mm I.D. silica tubing which is equivalent to 18 m of 0.25 m I.D.).

In: Back SS Inlet He, Out: Vacuum, Control mode – On – checked

Flow – checked – 1.3 ml min^{-1} i.e. constant flow method, Pressure – not checked ~25 psi (Note: this is the pressure at 35 °C, at 300 °C it will be ~55 psi)

Average velocity = 24.57 cm sec^{-1}, Hold up time = 5.29 min

Initial value 1.3 ml min^{-1}, run time 62 min, Post run: 1.3 ml min^{-1}

Oven – oven temp on – checked, Equilibration time: 0.1 min

Maximum oven temperature.: 325 °C, Override column max – 325 °C – not checked

Initial: 35 °C, hold time 1 min, ramp 1: 2 °C min^{-1} to 75 °C, hold time 0, ramp 2: 5 °C min^{-1} to 140 °C, hold time 0, ramp 3: 10 °C min^{-1} to 300 °C, hold time 12 min (62 min run)

Post run: 35 °C, post run time 0 min.

Detectors - FID front – nothing checked

Events – no entries

Signals – front signal (FID) – Data Rate 20 Hz, Min peak width 0.01 min (neither 'zero' nor 'save' checked).

Diagnostics: Test plot – Data Rate 50 Hz. Min peak width: 0.004 min – save checked.

Diagnostics: Back Inlet (SS Inlet): Flow: Actual, – Data Rate 50Hz. Min peak width: 0.004 min – save checked.

Configuration – Miscellaneous – pressure units: psi, Oven: slow fan – not checked, other entries 'not installed'.

Columns – 1 – Agilent 325 °C, 78 m x 250 µm x 0.25 µm DB-5 – Not inventoried, uncalibrated, back inlet, outlet: vacuum, heated by: oven.

Modules: Front inlet - SS inlet: He, Back inlet: He, Front detector FID, Makeup: He, Lit. Offset: 2.0 pA., ALS – No injectors

Counters – EMF counters – Nothing checked

Readiness – oven, front inlet, back inlet, front detector - all checked

GC Detector Data – Signal 3 display checked, atten: -2, Offset: 10 %, time: 10 min

Select Reports – none checked

TOF conditions:

In ProtoTOF 'Remote Control' 'Settings Mass Spectrometer/Measurements' Select:

1) 'Voltages' tab:

Transfer line heating = 230 °C (increased from 200 °C, October 21012)

Ion source heating = 230 °C (increased from 200 °C, October 2012)

2) 'scans and scansets' tab:

Scan range = 35-450 amu (changed from 20-450 amu October 2012 on advice of Markes)

AD trig delay = 20000

Scan Period = 100

Prescan/Scanset = 1

Scans/Scanset = 4500

Scanset Pause = 3000 (this gives a scanset rate of 2.2 Hz)

3) ‘Measurement’ tab:

‘Continuous’ checked

‘Filament delay’ checked, 300 seconds

Filament voltage = 1.7V

Time to wait for automatic safe standby = 3600 seconds

A.6.11 Calibration and quality control

As in A.5.10.

A.6.12 Processing of results

1) To export quantitated results: ‘File’ ‘Export data to CSV file’ ‘Current File – Select Destination’ ‘Quant/Unquant Results’, either choose a name or leave as default ‘Quant tab.csv’, choose a destination, say ‘My Documents’. If get message ‘File.....CSV exists. Append to it?’ Say ‘No’.

2) In Excel, open the file (check correct extension is selected). Copy and paste the required information into your spreadsheet.

A.7 Determination of formaldehyde released from materials using the acetylacetone method with fluorescence detection

A.7.1 Aim

This procedure describes the determination of formaldehyde released from materials using a screening technique (the FLEC). Air is drawn through gas washing bottles containing water which absorbs the formaldehyde. The analysis method is based on the Hantzsch reaction in which formaldehyde reacts with ammonium ions and acetylacetone to yield diacetyldihydrolutidine. The formaldehyde content is determined fluorimetrically. This procedure is based on the standard method BS EN 717-1:2004 for determination of formaldehyde release from wood-based panels.

A.7.2 Materials and equipment

1) Fluorimetric spectrophotometer (a Varian Cary Eclipse Fluorescence Spectrophotometer has been found to be suitable)

2) Water bath, capable of maintaining a temperature of 40 ± 1 °C (a Fisher Scientific ET150 BS5 has been found to be suitable)

3) Volumetric flasks, 100 and 1000 ml

4) Eppendorf pipettes, 1- 10 ml

5) 50 ml round bottom flasks

6) Balance, four decimal places

7) Gas washing bottles

8) Silica gel (for drying the air)

9) Acetylacetone

10) Ammonium acetate

11) Formaldehyde sodium bisulfite

12) Supply of pure water (that supplied by the Millipore Direct Q has been found to be suitable)

13) Air sampling pump (a Casella TUFF Plus Personal Air Sampler, fitted with a low-flow adaptor, has been found to be suitable).

14) Electronic flow meter (a TSI 4100 Series in-line flow calibrator has been found to be suitable)

A.7.3 Related document

1) European Standard BS EN 717-1:2004 "Wood-based panels – Determination of formaldehyde release – Part 1: Formaldehyde emission by the chamber method".

A.7.4 Preparation of reagents

1) The acetylacetone solution is prepared by adding 4 ml of acetylacetone to a 1,000 ml volumetric flask and making up to the mark with water.

2) The ammonium acetate solution is prepared by dissolving 200 g of ammonium acetate solution in water in a 1,000 ml volumetric flask and making up to the mark.

3) The formaldehyde standard solution is prepared by accurately weighing about 4.4703 g of formaldehyde sodium bisulfite, then dissolving it in water in a 1,000 ml volumetric flask and making up to the mark. The calibration solution is prepared by transferring 1 ml of the standard solution to a 1,000 ml volumetric flask and making up to the mark with water.

A.7.5 Sampling

1) 20 ml of purified water is added to each of two gas washing bottles which are then connected to each other (note that this is modified from 25 ml specified in the standard method in order to improve the detection limit of the method). Using the minimum length of plastic tubing possible, the inlet of the first in line bottle is connected to the outlet of the FLEC using an empty stainless steel tube. (Alternatively the bottle can be connected to the rear end of a sorbent tube if undertaking a trial of breakthrough of the novel method). The outlet of the second in line bottle is connected to a further gas washing bottle containing silica gel. The outlet of the drying bottle is connected through a flow meter to an air sampling pump.

2) The air exiting the FLEC is drawn through the gas washing bottles using an air sampling pump. A flow rate of up to 2 l min^{-1} can be used with this sampling method, but is limited here due to the flow which can be supplied by the FLEC air supply and also if concurrent sampling with another technique is being undertaken.

3) 10 ml of each of the absorption solutions is pipetted into a 50 ml flask and 10 ml of acetylacetone solution and 10 ml of ammonium acetate solution are added.

4) The flask is stoppered and heated for 15 minutes in a water batch at 40 °C. The flask is then wrapped in aluminium foil and placed in a cupboard and left for 1 hour.

5) A blank value is determined in parallel, using a solution made up of 10 ml water, 10 ml acetylacetone and 10 ml ammonium acetate solution.

A.7.6 Calibration

1) Dilutions of the calibration solution are made by pipetting either 1 ml, 3 ml, 5 ml, 10 ml, 20 ml or 50 ml into a 100 ml volumetric flask and making up to the mark with water. 10 ml of each are added to separate 50 ml flasks and treated as the sample solutions. The absorbance values obtained on analysis are plotted against the formaldehyde concentrations (see Figure A-1 for an example of a calibration curve obtained in March 2013).

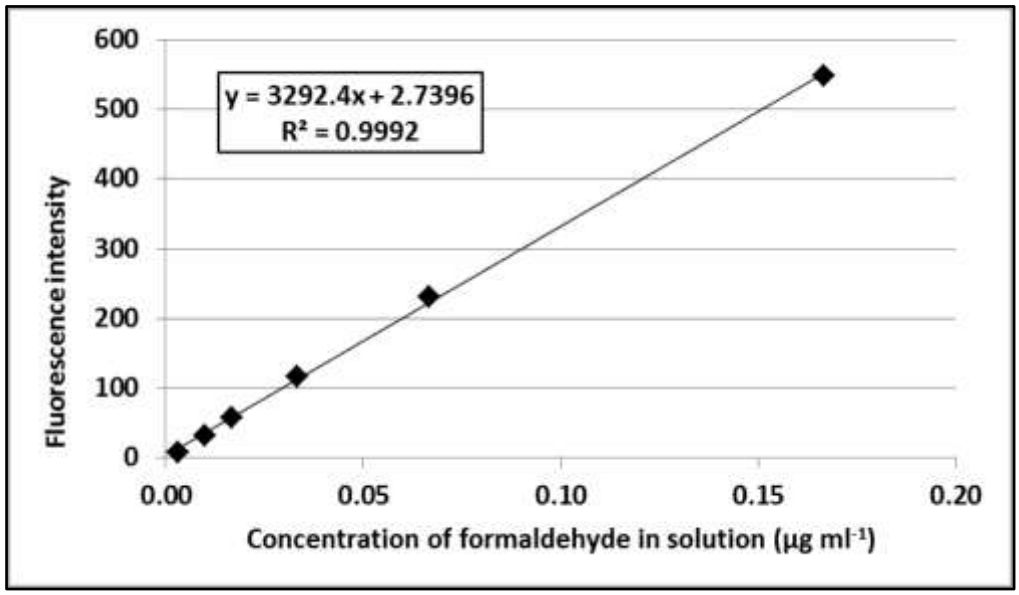

Figure A-1 Example of a calibration curve for formaldehyde determined by acetylacetone method using fluorimetric detection

A.7.7 Analysis

1) Switch on the instrument and PC and double click on 'scan'. If instrument says 'connect', click on this, if it says 'start' click on 'OK'.

2) Check 'status display' for current settings. Set excitation wavelength to 410 nm, wavelength range 420-600 nm, excitation and emission slits at 10, PMT at high, speed at medium.

3) Pipette sample or standard solution into a cuvette so that the top of the liquid is at the top of the holder unit. Wipe the outside of the cuvette and check for bubbles. Plastic cuvettes are OK for this method, but they must be clear on all four sides (not ridged).

4) Press 'start' and name the sample when prompted to do so.

5) When run has finished record intensity at 510 nm.

A.7.8 Calculation of formaldehyde concentration

1) The amount of formaldehyde absorbed in the water of the gas washing bottle is calculated by the following equation:

$G = (As - Ab) \times f \times Vs$

where G is the amount of formaldehyde in the trapping solutions (in μg), As is the absorbance of the solution from the gas washing bottle, Ab is the absorbance of the blank value, f is the slope of the calibration curve (mg ml^{-1}) and Vs is the volume of the trapping solutions (ml).

2) The concentration of formaldehyde in the air exiting from the FLEC is calculated by the following equation:

$C = G/Va$

where C is the formaldehyde concentration (in μg l^{-1}) and Va is the volume of the air sample (in litres).

Appendix B Tests undertaken to investigate performance of µ-CTE and FLEC

B.1 µ-CTE system background

Several control runs were undertaken during tests using the µ-CTE. For these the exit air from the µ-CTE was sampled with no materials in any of the chambers. The chromatograms obtained from analysis of the control samples showed a few small peaks due to artefacts of the sorbent. The possible contribution to the TVOC values in the analysis of the material samples is shown in Table B-1 which gives the total amount of VOCs found (in ng on the tube) over the TVOC range (C_6-C_{16}) for the control tubes analysed during testing of the wall covering materials in the µ-CTE. The table shows results separated according to the two sorbent types, Tenax TA and multi-sorbent, MS2, (quartz wool/Tenax TA/Carbopack X) used in these tests. It also shows values obtained for blank tubes (i.e. conditioned tubes not used for air sampling) for which one tube of each sorbent type was analysed per test.

In many cases the values are below the limit of quantification (5 ng on the tube per compound as a toluene equivalent), but small amounts of one or more compounds can occur at levels which need to be controlled for during TVOC calculations. Analysis of re-collected blank tubes is seen to give a somewhat higher background level which was found to be due to a higher benzene value. This therefore would need to be taken into account if re-collected tubes are to be used for the measurement of benzene and/or TVOCs. The results suggest that a control sample may give a higher background than a blank sample, suggesting that the passing of air over the tubes can increase the artefact level. It is important to run regular control samples in any case as a check on the cleanliness of the chambers. The results also suggest that background levels for the MS2 tubes may be slightly, but not dramatically, higher than those for Tenax TA only tubes.

Table B-1 Blank and control levels found during µ-CTE sampling

Experiment Date	Details	TVOCs (ng on the tube)		Compounds detected
		Tenax	MS2	
05/07/2011	Control run, 23 °C	9.0-32.5	6.3-15.6	HMCTS [1], nonanal, decanal
05/07/2011	Control run, 40 °C	11.6-129	12.1-16.6	Benzene, HMCTS, nonanal, decanal
06/07/2011	Blank tubes	ND [2]	6.1	HMCTS
07/07/2011	Blank tubes	ND	11.7	Acetaldehyde, benzene
08/07/2011	Blank tubes	ND	ND	-----
08/07/2011	Analysis of re-collected blank tubes	21.5	31.2	Benzene, HMCTS
11/07/2011	Blank tubes	ND	ND	-----
11/07/2011	Control run, 40 °C	ND	ND-6.9	HMCTS
13/07/2011	Blank tubes	ND	ND	-----
13/07/2011	Analysis of re-collected blank tubes	45.8	52.3	Benzene, HMCTS, benzaldehyde, benzoic acid
20/07/2011	Blank tubes	ND	ND	-----
20/09/2011	Blank tubes	5.5	6.7	HMCTS, decanal
20/09/2011	Control run, 40 °C	ND	ND-11.6	HMCTS
21/09/2011	Blank tubes	ND	5.7	HMCTS
22/09/2011	Blank tubes	ND	ND	-----
22/09/2011	Control run, 23 °C	ND	ND-16.8	HMCTS
26/10/2011	Blank tubes	ND	ND	-----
26/10/2011	Control run, 23 °C	ND	ND	-----

[1] HMCTS = hexamethylcyclotrisiloxane; [2] ND = not detected

B.2 FLEC system background

One end of a Supelco filter unit which had been freshly charged with Supelpure® pure adsorbent (activated charcoal) was connected to the laboratory compressed air supply. The other end of the filter was connected to the air supply inlet of the FLEC air control unit using 1/8th-inch copper tubing. The combined air outlet at the front of the air control unit was connected to the inlet orifice of the FLEC using 1/4-inch PFA

(Perfluoroalkoxy) tubing. The FLEC was placed on the empty carpet test plate and air was allowed to flow through the system. A number of tests of the amounts of VOCs found at various points of the system were then undertaken while the apparatus was being flushed over a period of several days.

The TVOC background concentrations in the FLEC, recorded after it had been connected to the air supply via the air control unit, are shown in Table B-2. The table also shows the compounds which are contributing to the TVOC levels. Some fairly high values were recorded initially but there was a general decline in concentration with continuing operation. The control samples taken before the emission tests of the four wall covering materials and before the recovery test all had acceptable background levels (i.e. <20 µg m^{-3}), which were in each case due to the presence of either one or a few contaminants. In order to identify the point in the system which was contributing most to the background levels, some samples were also taken from the dry, humid and combined outlets of the air control unit. The humid air outlet was found to give higher TVOC concentrations than the dry and combined air outlets. When there was no water in the unit the TVOC concentration from the humid air outlet was below the limit of quantification, which suggests that the presence of water is the major contributor to TVOCs in the background air. If TVOC background levels became an issue it would therefore be necessary to investigate the quality of the water used in the system.

Table B-2 TVOC background concentrations in FLEC

Date	Testing point/details	TVOC concentration (µg m^{-3})	Compounds detected
20/07/11	FLEC outlet	25.8, 27.8	2-ethylhexan-1-ol, dimethylbenzene methanol [1], nonanal, n-dodecane, decanal, a C_{12} siloxane, BHT
21/07/11	FLEC outlet	10.5, 9.6	dimethylbenzene methanol [1], nonanal, 2 x aliphatic hydrocarbons
21/07/11	Air control outlet	20.1 (dry and humid combined)	dimethylbenzene methanol [1], nonanal, decanal, 2 x aliphatic hydrocarbons
25/07/11	FLEC outlet	34.7, 49.3	hexanal, n-decane, HMCTS [2], dimethylbenzene methanol [1], nonanal, n-dodecane, decanal, phenol, an aliphatic hydrocarbon
25/07/11	Air control outlet	6.7 (combined)	dimethylbenzene methanol [1], nonanal, decanal, an aliphatic hydrocarbon
26/07/11	FLEC outlet (pre-wall covering 4)	5.0, 5.5	nonanal, 2 x aliphatic hydrocarbons
01/08/11	Air control outlet	2.8 (dry), 17.2 (humid), 4.2 (combined)	dimethylbenzene methanol [1] (humid only), HMCTS, nonanal, decanal
02/08/11	FLEC outlet (pre-wall covering 1)	7.1, 6.4	HMCTS, nonanal, decanal, an aliphatic hydrocarbon
09/08/11	FLEC outlet (pre-recovery test)	12.5, 11.6	HMCTS, m/p-xylene, nonanal, decanal, an aliphatic hydrocarbon
11/08/11	Air control outlet	2.6 (dry), 21.5 (humid), 13.1 (combined)	nonanal (all), HMCTS, decanal, an aliphatic hydrocarbon (humid and combined)
26/08/11	Air control outlet (no water in unit)	Not detected (<1 µg m^{-3} for each compound, dry and humid)	--------
02/09/11	Air control outlet (water re-added)	2.8 (dry), 16.4 (humid)	nonanal, decanal (dry), HMCTS, OMCTS [3], a C_{12} siloxane, an aliphatic hydrocarbon (humid)
06/09/11	FLEC outlet (pre-wall covering 3)	2.7, 0.5	HMCTS, nonanal, decanal
27/09/11	FLEC outlet (pre-wall covering 2)	1.7, 0.9	HMCTS

[1] tentative identification; [2] HMCTS = hexamethylcyclotrisiloxane;
[3] OMCTS = octamethylcyclotetrasiloxane

B.3 Temperature of laboratory during FLEC tests

The temperature of the laboratory was recorded during emissions tests using spot measurements while air samples were taken from the FLEC. Several periods of temperature logging were also undertaken using either an Extech CO2/Humidity/ Temperature Datalogger SD8000, a Gemini Tinytalk temperature logger or a Gemini TinyTag View 2 temperature and humidity logger. The temperatures recorded in the laboratory using the three different temperature monitoring devices are shown in Figure B-1. The temperature was fairly stable with fluctuations of up to only about 5 °C (between 19 and 24 °C). This was considered acceptable for a non-certified test, but a narrower control of temperature (23 ±2 °C) would be required to meet the requirement in ISO 16000-10:2006. For this it may be necessary to place the apparatus in a controlled temperature room.

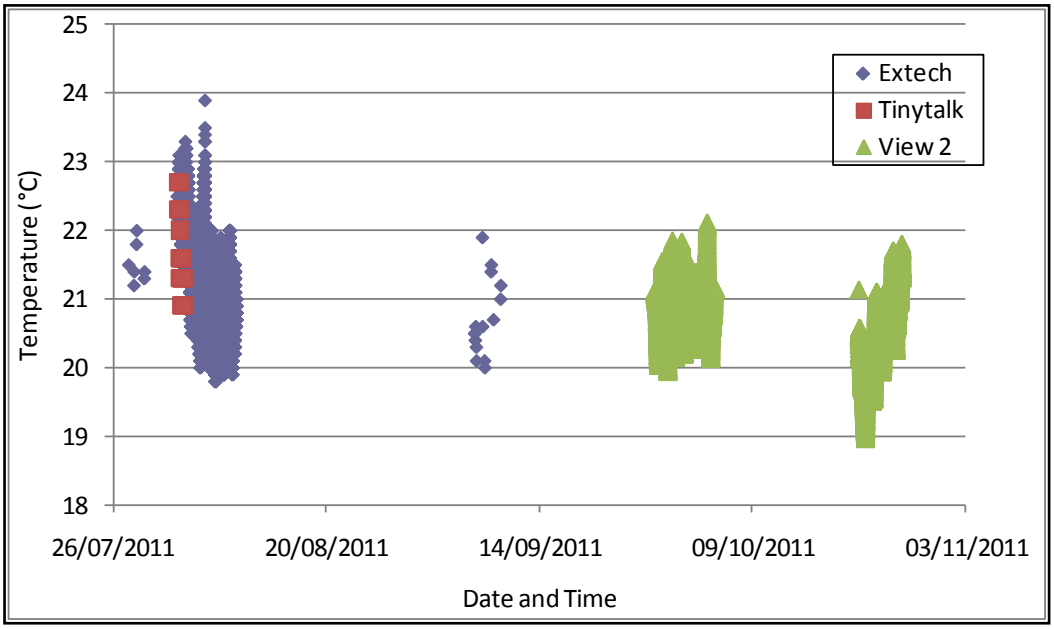

Figure B-1 Temperature of the laboratory during the FLEC tests of wall covering materials

B.4 Humidity supply to FLEC

The humidity supplied by the FLEC air control unit was tested by placing a Gemini TinyTag View 2 temperature and humidity logger inside a glass desiccator and placing

the FLEC over the desiccator. The air flow from the air control unit dry air and humid air outlets were each set at 119 ml min^{-1}, giving a total air flow from the air control outlet of 238 ml min^{-1}. The air flow at the outlet of the FLEC was recorded as 237 ml min^{-1} showing that the seal between the FLEC and the desiccator was airtight. The logger was left in the desiccator for 30 minutes with air flowing through the system and at the end of this time the humidity reading was noted to be 51.6 %RH. This shows that the air control unit is operating correctly as with both the dry and humid air controllers set to give the same flow, the air exiting the air control unit should have a relative humidity of 50 %. The ISO 16000-10:2006 standard requires emission tests to be undertaken at 50 ±5 %RH so the unit is able to supply air within the required tolerance for relative humidity.

B.5 Recovery through FLEC

ISO 16000-10:2006 specifies undertaking recovery tests through the FLEC using n-dodecane and toluene. A source of n-dodecane was established by weighing an aliquot of the neat chemical into the 2 ml ground glass vial included with the recovery test kit. The vial was kept open to the atmosphere within a fume cupboard and re-weighed several times over a period of two weeks. It was then fitted into the recovery test kit and this was placed under the FLEC. Dry air was passed through the FLEC at a flow rate of 260 ml min^{-1}. The source was removed briefly from under the FLEC to be weighed twelve times over a period of three weeks. Three duplicate samples of the air exiting from the FLEC were taken during this time, allowing a minimum of 7 hours from the time the source was removed from the FLEC for weighing to the time of sampling. The supply air was then adjusted to give a relative humidity of 50 % and the source was weighed a further four times over a ten day period. Three duplicate air samples were again taken from the air exiting the FLEC during this time, allowing at least five hours from the time of weighing the source to the time of sampling. The sampled sorbent tubes were analysed using the TD-100/GC/MSD and the amount of n-dodecane present was quantified.

The mass loss from the n-dodecane source over the duration of the test is shown in Figure B-2. This shows no significant difference in mass loss between the dry and 50 % humid atmospheres. The expected n-dodecane concentration over the period that dry air

was passed through the FLEC was calculated to be 3,304 µg m^{-3}. The mean concentration recorded over the three sampling periods was 3,042 µg m^{-3}, giving a recovery of 92 %. For the period that humid air was passed through the FLEC the expected concentration of n-dodecane was 3,220 µg m^{-3} and the mean concentration recorded over the three sampling periods was 2,686 µg m^{-3}, giving a recovery of 83 %. ISO 16000-10:2006 states that the recovery for n-dodecane through the FLEC should be greater than 80 %, so acceptable recovery has been achieved in this test. Further tests would be required to confirm whether the presence of humidity is resulting in a consistently lower recovery for n-dodecane through the system.

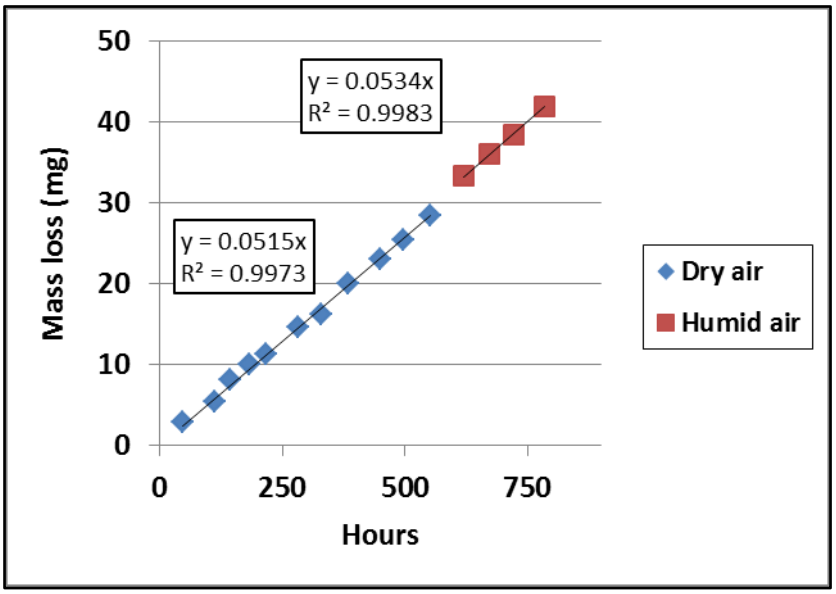

Figure B-2 Cumulative mass loss from source of n-dodecane during recovery test

Appendix C Development of an optimised TD-100/GC/MSD procedure and performance of the system

C.1 TD-100 settings

C.1.1 Cold trap packing

During analysis, VOCs are concentrated on the cold trap within the thermal desorber, before they are vaporised and introduced onto the GC column. The standard configuration for the TD-100 cold trap is so called 'backflush' mode in which the flow of helium during trap desorption is the reverse of that during tube desorption. The selection of cold trap packing material is important for the range of compounds which can be determined. For this project, in order to optimise the volatility range for compounds emitted from materials, a cold trap containing quartz wool followed by Tenax TA and finally the graphitised carbon Carbograph 5TD (known as a 'materials emissions' cold trap) was selected.

C.1.2 Gas flow rates

Gas flow rates and split ratios are important parameters for defining the sensitivity of the analytical method. There are two points during the analysis at which the sample may be split, tube desorption and trap desorption. As some compounds, for example carcinogens, are required to be determined with high sensitivity, it was decided to have no split set during tube desorption and to investigate the minimum split flow which gives repeatable results during trap desorption. The system was initially set up with a 0 to 100 ml min^{-1} mass flow controller (MFC) controlling the desorb flow and a 0 to 200 ml min^{-1} MFC controlling the split/re-collection flow. The effective working range for MFCs is stated to be from 5 % of the maximum flow, so this would mean a minimum recommended flow rate of around 10 ml min^{-1} for the split/re-collection MFC and 5 ml min^{-1} for the desorb MFC.

ISO 16000-6:2011 states that typical tube desorption gas flow rates for VOC analysis are 30 ml min^{-1} to 50 ml min^{-1}. In order to assist desorption of high boiling compounds

the MFC controlling the tube desorption flow rate was set at 50 ml min^{-1}, which is well within the recommended range for a 0-100 ml min^{-1} flow controller.

The flows obtained at a range of settings of the 0-200 ml min^{-1} controller were checked by varying the settings in the TD-100 software while measuring the flow at the appropriate outlet at the front of the instrument using an Agilent ADM2000 flow meter. The results obtained are shown in Figure C-1. The flows obtained are very close to the set values. Values recorded at settings below 10 ml min^{-1} did show greater variability, so it was expected that 10 ml min^{-1} as the split flow during analysis would be the minimum setting to give reliable flows and maximum sensitivity.

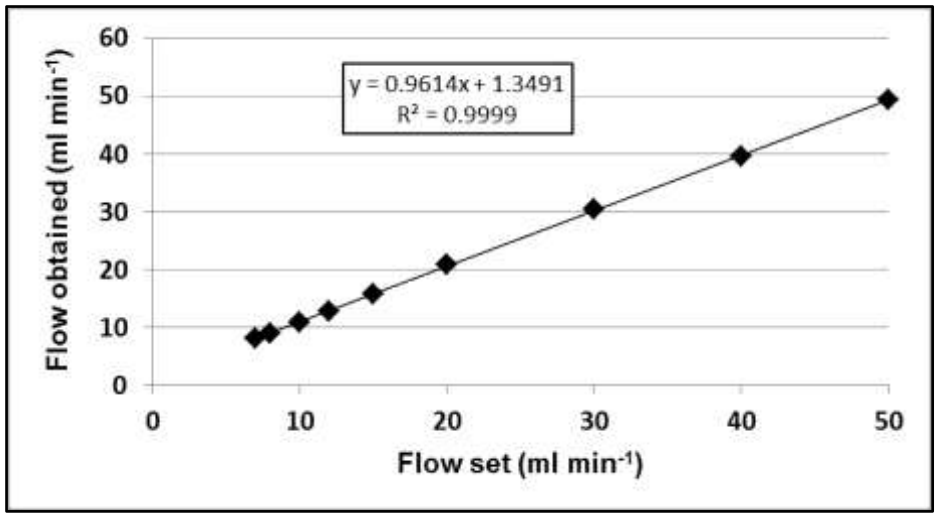

Figure C-1 Check of calibration of 0-200 ml min^{-1} mass flow controller

In order to investigate the minimum setting for the split flow during trap desorption which gives repeatable results, five repeat injections of a standard solution containing 80 ng μl^{-1} of each of seven VOCs in methanol were analysed using a split flow of 10 ml min^{-1}. Further sets of five repeats were analysed with split flows of 12.5, 15 and 20 ml min^{-1}. The results obtained from analysis of these sets of repeat standard solutions are shown in Table C-1. A significantly higher variability was found in the results obtained with a split flow of 10 ml min^{-1} than when it was set at any of the higher values, particularly for the more volatile compounds. For the initial arrangement of the MFCs, a split flow of 12.5 ml min^{-1} was therefore employed to maximise sensitivity without compromising repeatability.

Table C-1 Investigation of repeatability with different split flows and 0-200 ml min^{-1} mass flow controller regulating the split flow

Compound	Extracted ion peak area											
	Split flow at 10 ml min^{-1}			Split flow at 12.5 ml min^{-1}			Split flow at 15 ml min^{-1}			Split flow at 20 ml min^{-1}		
	Mean	SD	% RSD	Mean	SD	% RSD	Mean	SD	% RSD	Mean	SD	% RSD
n-Hexane	1,052,270	991,564	94.2	2,150,364	41,159	1.9	1,839,968	82,775	4.5	1,561,744	47,608	3.0
Toluene	11,371,485	9,028,615	79.4	9,308,353	317,029	3.4	8,196,138	195,906	2.4	6,899,024	94,378	1.4
m-Xylene	10,134,191	7,204,565	71.1	8,005,620	124,675	1.6	7,003,774	116,885	1.7	5,895,484	95,449	1.6
Limonene	4,523,556	2,476,959	54.8	3,234,427	33,996	1.1	2,808,087	45,062	1.6	2,366,093	38,123	1.6
2-Ethyl-hexan-1-ol	6,123,642	3,127,892	51.1	4,224,930	116,627	2.8	3,785,715	18,306	0.5	3,104,547	64,252	2.1
Naphthalene	25,804,252	4,293,652	16.6	13,146,426	227,804	1.7	11,459,704	231,469	2.0	9,741,308	156,586	1.6
n-Hexadecane	7,126,948	1,16,912	15.7	4,299,845	64,935	1.5	3,743,982	57,251	1.5	2,566,586	277,352	10.8

The benefit of switching the MFCs so that the 0-100 ml min^{-1} MFC controls the split flow was also investigated, with further repeat analyses of the standard solution being undertaken at a range of split flows using this arrangement. After switching the mass flow controllers, calibration against the electronic flow meter again gave good correlation (Figure C-2). Initially, however, poor repeatability was obtained on repeat analysis of standard solutions with split flows of 7.5 - 20 ml min^{-1}, whilst repeatability was significantly better using a split flow of 50 ml min^{-1}. Table C-2, for example, shows the results obtained on analysis of 10 repeat standard solutions using a split flow of 50 ml min^{-1}. The split flow was re-collected onto the same set of tubes and these were then re-analysed using a split flow of 12.5 ml min^{-1}. This experiment was repeated using a set of tubes which had been spiked with the same standard solution and analysed at Markes International's laboratory with re-collection of the split flow. Good results had been achieved at Markes (%RSD < 10%). Good repeatability was also obtained at Cranfield for these tubes using a split flow of 50 ml min^{-1}, but repeatability was poorer at 12.5 ml min^{-1} (Table C-3). Following discussion with chromatography specialists at Markes, the split/re-collection needle valve at the front of the instrument, which had been set at value of >100 ml min^{-1}, was set to limit the flow to a maximum of 60 ml min^{-1}. Results obtained for further sets of five repeat standard solutions analysed with split flows during trap desorption of between 5 and 10 ml min^{-1} all then showed good repeatability (Table C-4).

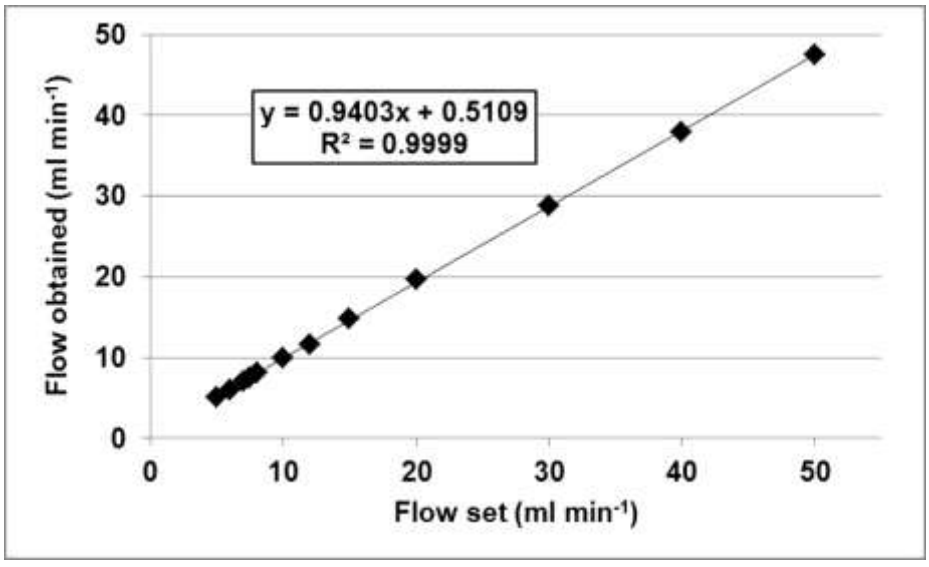

Figure C-2 Check of calibration of 0-100 ml min^{-1} mass flow controller

Table C-2 Investigation of repeatability with different split flows and 0-100 ml min^{-1} mass flow controller regulating the split flow – tubes spiked at Cranfield

Compound	Extracted ion peak area					
	Split flow at 50 ml min^{-1}			Split flow at 12.5 ml min^{-1}		
	Mean	SD	%RSD	Mean	SD	%RSD
n-Hexane	666,591	30,143	4.5	1,482,780	322,404	21.7
Toluene	3,742,314	124,151	3.3	9,096,016	1,603,594	17.6
m-Xylene	3,283,768	97,211	3.0	8,040,076	1,141,354	14.2
Limonene	1,177,898	31,103	2.6	2,700,317	351,792	13.0
2-Ethyl-hexan-1-ol	1,658,903	60,278	3.6	4,120,109	626,671	15.2
Naphthalene	6,079,543	198,326	3.3	15,494,720	2,275,437	14.7
n-Hexadecane	2,139,832	89,652	4.2	5,520,266	563,816	10.2

Table C-3 Investigation of repeatability with different split flows and 0-100 ml min^{-1} mass flow controller regulating the split flow – tubes spiked at Markes

Compound	Extracted ion peak area					
	Split flow at 50 ml min^{-1}			Split flow at 12.5 ml min^{-1}		
	Mean	SD	%RSD	Mean	SD	%RSD
n-Hexane	499,014	39,842	8.0	1,276,644	174,450	13.7
Toluene	3,113,596	72,222	2.3	7,970,469	1,295,854	16.3
m-Xylene	2,828,024	29,857	1.1	7,082,818	727,167	10.3
Limonene	1,022,511	13,778	1.3	2,575,611	189,263	7.3
2-Ethyl-hexan-1-ol	1,383,627	27,577	2.0	3,817,296	228,660	6.0
Naphthalene	5,183,449	35,972	0.7	15,358,682	1,894,261	12.3
n-Hexadecane	1,866,061	128,252	6.9	5,264,625	551,139	10.5

Table C-4 Investigation of repeatability with different split flows and 0-100 ml min^{-1} mass flow controller regulating the split flow (needle valve set at 60 ml min^{-1})

Compound	Extracted ion peak area					
	Split flow at 10 ml min^{-1}		Split flow at 7.5 ml min^{-1}		Split flow at 5 ml min^{-1}	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
n-Hexane	2,155,884	3.9	1,881,014	2.4	2,496,260	3.8
Toluene	8,633,650	1.3	7,902,842	3.0	10,514,494	2.7
m-Xylene	8,055,246	0.9	7,568,642	3.3	9,990,277	3.0
Limonene	3,195,884	1.6	2,803,837	2.8	3,768,711	2.7
2-Ethyl-hexan-1-ol	6,350,610	1.7	6,929,692	2.8	9,425,637	4.7
Naphthalene	12,663,650	1.2	12,642,770	3.5	16,771,136	2.0
n-Hexadecane	7,924,187	1.5	8,817,861	1.5	11,804,688	3.6

With this arrangement of MFCs therefore, good results are achievable using split flows down to 5 ml min^{-1}. To aid the analysis of high boiling compounds, however, a minimum split flow of 10 ml min^{-1} during trap desorption is recommended so it was decided to retain the 0-100 ml min^{-1} MFC for control of split flows and to use a value of 10 ml min^{-1}.

C.1.3 Flow path temperature

Typical flow path temperatures for analysis of volatile compounds using the TD-100 are 120 °C to 150 °C, but 200 °C to 210 °C are required for analysis of SVOCs (Markes, 2005). For this project, in order to optimise the analysis of high boilers, it was therefore decided to investigate the use of 200 °C – 210 °C as the flow path temperature.

C.1.4 Desorption conditions

ISO 16000-6:2011 states that desorption conditions should be selected so that the desorption efficiency for n-octadecane is better than 95 %. Typical conditions suggested in this standard for VOC analysis are a desorption temperature of 260 °C to 280 °C and desorption time of 5 to 15 minutes. For this project it was decided to investigate whether there is any advantage for desorption of higher boiling compounds in using

more stringent desorption conditions. 320 °C is normally recommended as the maximum desorption temperature for Tenax TA and 330 °C as the maximum conditioning temperature (Markes, 2012). Repeat analyses of several mixtures of VOCs, including n-octadecane and some other high boiling compounds, were undertaken using a range of desorption temperatures and desorption times in order to determine the optimum desorption conditions.

Potential carry-over of a mixture of VOCs including n-octadecane (VOC mix 1) was investigated by analysing the mixture which had been spiked onto a Tenax TA tube followed by analysing an empty tube and then re-desorbing the Tenax TA tube. This procedure allows any carry-over in the system and on the tube to be identified separately. The tube desorption conditions used for each of these analyses were 300 °C for 8 minutes with a flow rate of 50 ml min^{-1} and trap desorption conditions were a cold trap high temperature of 300 °C for 3 minutes. Results obtained are shown in Table C-5.

Table C-5 Investigation of carry-over of compounds in VOC mix 1 on analysis using the TD-100/GC/MSD system

Compound	Extracted ion peak area (n = 1)			% carry-over		
	1st Desorption	Empty tube	2nd Desorption	In system	On tube	Total
Butan-2-ol	80,783,720	56,571	ND [1]	0.1	ND	0.1
Octanoic acid	40,748,724	360,377	ND	0.9	ND	0.9
n-Octadecane	527,373,219	139,249	ND	<0.1	ND	<0.1

[1] ND = not detected

No carry-over of any of the three compounds was observed on the second desorption of the tube, and <1 % carry-over was seen in the system. Therefore both n-octadecane, which has a boiling point of 317 °C, and octanoic acid, which has a lower boiling point of 240 °C but is a 'stickier' compound, are being desorbed effectively using the current conditions. This experiment was repeated with a different mixture of compounds (VOC mix 2) including phenanthrene (boiling point 340 °C) and dodecyl benzene (boiling point 331 °C). Performance was first investigated for three Tenax TA tubes using the desorption conditions employed in the experiment above and a further three tubes which were desorbed at 320 °C for 12 minutes followed by a cold trap high temperature of

320 °C for 5 minutes. Each tube was spiked with approximately 1,000 ng of each compound and for all these analyses a flow path of 200 °C was used. Mean % carry-over for the different desorption conditions are shown in Table C-6. No advantage was found for these compounds in using the more stringent desorption conditions.

Performance was then investigated for three Tenax TA tubes and three multi-sorbent tubes, MS2 (see Section 2.3.1) each spiked with approximately 1,000 ng of each compound. These tubes were analysed with the desorption conditions used in the first desorption experiment and a flow path temperature of 210 °C. Results obtained for the different compounds with each type of tube are shown in Table C-7. All compounds other than phenanthrene exhibited carry-over of <0.5 % in the system and ≤0.5 % on the tube, while carry-over for phenanthrene was <2 % in the system and <1 % on the tube. No significant difference in % carry-over was observed between the two sorbent types. The higher flow path temperature does not appear to have made a significant difference for these compounds, but it was decided to keep the flow path at 210 °C to aid desorption of very high boiling components.

Table C-6 Investigation of carry-over of compounds in VOC mix 2 using Tenax TA tubes and different desorption conditions

Compound	Mean % carry-over					
	Desorb at 300 °C for 8 min, cold trap high 300 °C for 3 min (n = 3)			Desorb at 320 °C for 12 min, cold trap high 320 °C for 5 min (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Cyclohexane	ND	<0.1	<0.1	<0.1	0.2	0.2
1,4-Dioxane	0.1	0.3	0.4	0.3	0.3	0.6
Butyl acrylate	<0.1	0.1	0.1	<0.1	<0.1	<0.1
2-(2-Ethoxyethoxy)-ethanol	0.2	0.1	0.3	<0.1	0.1	0.1
Octan-1-ol	0.2	0.1	0.3	0.1	<0.1	0.1
Phenanthrene	1.4	0.7	2.1	1.6	0.9	2.5
Dodecyl benzene	0.4	0.1	0.5	0.4	0.2	0.6

Table C-7 Investigation of carry-over of compounds in VOC mix 2 using different sorbents

Compound	Mean % carry-over using the conditions: desorb at 300 °C for 8 min, cold trap high 300 °C for 3 min, flow path 200 °C					
	Tenax (n = 3)			MS2 (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Cyclohexane	ND	ND	ND	ND	ND	ND
1,4-Dioxane	0.1	0.2	0.3	0.1	0.5	0.6
Butyl acrylate	0.1	0.1	0.2	<0.1	<0.1	<0.1
2-(2-Ethoxyethoxy)-ethanol	0.1	<0.1	0.1	<0.1	0.1	0.1
Octan-1-ol	0.1	0.1	0.2	0.1	0.1	0.2
Phenanthrene	1.3	0.6	1.9	1.6	0.8	2.4
Dodecyl benzene	0.4	0.1	0.5	0.4	0.2	0.6

Further experiments were undertaken with a mixture containing several compounds including dibutyl phthalate (boiling point 340 °C) and di-2-ethylhexylphthalate (DEHP, boiling point 384 °C) (VOC mix 3). Performance was first investigated by analysis of approximately 1,000 ng μl^{-1} of each of these compounds spiked onto two Tenax TA tubes using each of the sets of desorption conditions tested above. Mean % carry-over for each set of desorption conditions is shown in Table C-8. Carry-over for all of the compounds was found to be <1 % in the system and ≤0.5 % on the tube with no reduction in carry-over using the more stringent desorption conditions. It was therefore decided to use 300 °C for 8 minutes for tube desorption and 300 °C for 3 minutes for trap desorption.

Table C-8 Investigation of carry-over of compounds in VOC mix 3 using different desorption conditions

Compound	Mean % carry-over					
	Desorb at 300 °C for 8 min, cold trap high 300 °C for 3 min (n = 2)			Desorb at 320 °C for 12 min, cold trap high 320 °C for 5 min (n = 2)		
	In system	On tube	Total	In system	On tube	Total
Ethyl acrylate	0.1	0.3	0.4	0.1	0.4	0.5
Dimethylformamide (DMF)	ND	ND	ND	ND	ND	ND
2-Butoxyethyl acetate	0.1	ND	0.1	ND	0.1	0.1
Butylated hydroxy-anisole (BHA)	0.2	<0.1	0.2	0.2	0.1	0.3
Diethyl phthalate	0.7	0.2	0.9	0.7	0.3	1.0
2,2,4-Trimethylpent-anedioldiisobutyrate (TXIB)	0.5	0.1	0.6	0.4	0.1	0.5
Dibutyl phthalate	0.9	0.4	1.3	0.9	0.4	1.3
Di-2-ethylhexyl-phthalate (DEHP)	0.9	0.4	1.3	0.9	0.5	1.4

Carry-over of compounds in VOC mix 3 was further investigated by analysis of three Tenax TA tubes and three MS2 tubes using the selected desorption conditions. Each tube had been spiked with 1 µl of a solution containing approximately 300 ng of each compound. Results obtained are shown in Table C-9. Total carry-over in the system and on the tube was found to be <1 % for each of the compounds. The current system and conditions are therefore suitable for the analysis of some SVOCs including DEHP. As with the previous experiment, no significant difference was observed in performance between the two sorbent types. This suggests that use of the multi-sorbent tube does not compromise the analysis of the range of compounds investigated here. It needs to be borne in mind, however, that spiking of analytes onto a tube may not provide a stringent test of recovery of these chemicals from these tubes following air sampling. This is because spiking involves passing about 240 ml of gas through a tube, whilst typically 1 to 5 litres are passed through during air sampling. This could result in the analytes being differently distributed across the sorbents and potentially more

difficult to remove. The performance of the multi-sorbent tube is investigated further in Chapters 4 and 5.

Table C-9 Investigation of carry-over of compounds in VOC mix 3 using different sorbents

Compound	Mean % carry-over using the conditions: desorb at 300 °C for 8 min, cold trap high 300 °C for 3 min, flow path 200 °C					
	Tenax (n = 3)			MS2 (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Ethyl acrylate	ND	ND	ND	ND	ND	ND
DMF	ND	ND	ND	ND	ND	ND
2-Butoxyethyl acetate	ND	ND	ND	<0.1	0.1	0.1
BHA	0.2	ND	0.2	0.1	ND	0.1
Diethyl phthalate	0.5	0.2	0.7	0.5	0.2	0.7
TXIB	0.3	0.1	0.4	0.3	0.2	0.5
Dibutyl phthalate	0.6	0.3	0.9	0.6	0.3	0.9
DEHP	0.4	0.3	0.7	0.5	0.4	0.9

One issue with the use of Tenax TA as sorbent material is that analysis of a conditioned Tenax TA tube shows the presence of a small amount of benzene and this background does not decline with the number of times the tube has been used. It was therefore decided to check whether the size of the benzene background is affected by desorption temperature. Seven conditioned Tenax TA tubes were analysed using a desorption temperature of 280 °C, a further seven were analysed using a temperature of 300 °C and a further seven using a temperature of 320 °C. All other instrument parameters were the same. The amount of benzene obtained (Figure C-3) was found to increase slightly as the desorption temperature is increased to 300 °C and more sharply when a temperature of 320 °C is used. As benzene is a compound which is required to be determined to a low level in tests of material emissions, these results suggest that it would be advisable to use the minimum possible desorption temperature.

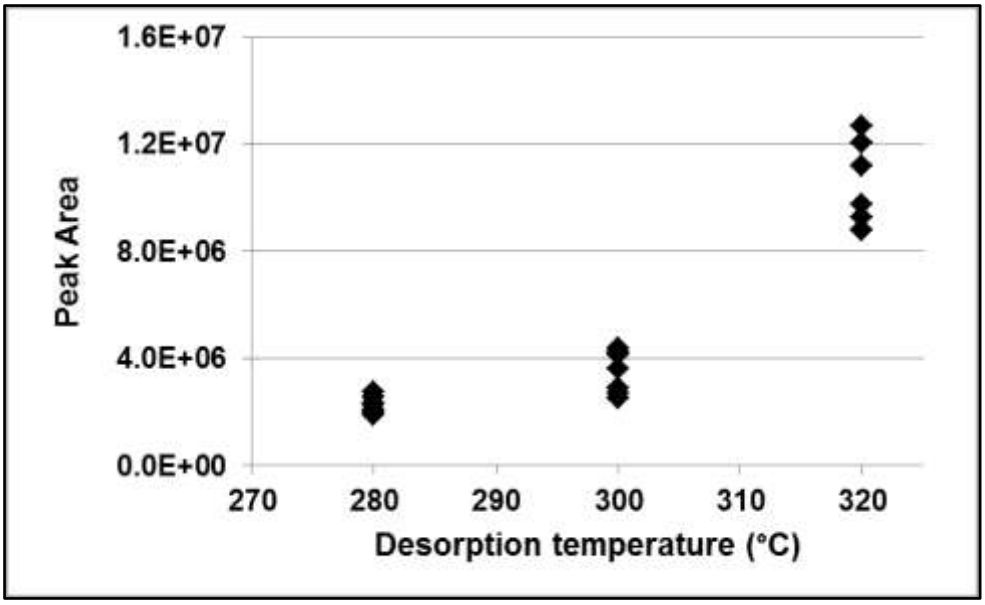

Figure C-3 Amount of benzene released from Tenax TA tubes desorbed at different temperatures

With the findings for benzene in mind, some further experiments were undertaken in which the carry-over of the compounds in VOC mix 2 and VOC mix 3 using both Tenax TA and MS2 tubes and a desorption temperature of 280 °C was investigated. Three tubes of each sorbent type and a loading of 300 ng were investigated and other desorption conditions were the same as employed previously. Mean % carry-over values for VOC mix 2 are shown in Table C-10 and those for VOC mix 3 are shown in Table C-11. With the exception of one tube for which some carry-over of 1,4-dioxane was observed, for both compound mixes the use of a desorption temperature of 280 °C resulted in a total carry-over of ≤ 1 %. The use of this temperature therefore results in acceptable performance for this range of compounds.

Table C-10 Investigation of carry-over of compounds in VOC mix 2 using a desorption temperature of 280 °C

Compound	Mean % carry-over using the conditions: desorb at 280 °C for 8 min, cold trap high 300 °C for 3 min, flow path 200 °C					
	Tenax (n = 3)			MS2 (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Cyclohexane	ND	ND	ND	ND	ND	ND
1,4-Dioxane	ND	1.5 [1]	1.5	ND	ND	ND
Butyl acrylate	ND	0.2	0.2	ND	ND	ND
2-(2-Ethoxyethoxy)-ethanol	ND	ND	ND	ND	ND	ND
Octan-1-ol	ND	ND	ND	ND	ND	ND
Phenanthrene	0.7	0.3	1.0	0.7	0.3	1.0
Dodecyl benzene	0.2	ND	0.2	0.2	ND	0.2

[1] Carry-over found on one tube only

Table C-11 Investigation of carry-over of compounds in VOC mix 3 using a desorption temperature of 280 °C

Compound	Mean % carry-over using the conditions: desorb at 280 °C for 8 min, cold trap high 300 °C for 3 min, flow path 200 °C					
	Tenax (n = 3)			MS2 (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Ethyl acrylate	ND	ND	ND	0.3	ND	0.3
DMF	ND	ND	ND	ND	ND	ND
2-Butoxyethyl acetate	ND	ND	ND	ND	ND	ND
BHA	<0.1	ND	<0.1	ND	ND	ND
Diethyl phthalate	0.3	0.1	0.4	0.2	0.2	0.4
TXIB	0.3	0.1	0.4	0.3	0.4	0.7
Dibutyl phthalate	0.3	0.1	0.4	0.2	0.1	0.3
DEHP	0.9	0.1	1.0	0.9	<0.1	0.9

A final desorption test investigated the benefit of use of a flow path temperature of 210 °C (the maximum possible temperature for the instrument). The carry-over from three Tenax TA tubes loaded with 300 ng of VOC mix 3 and desorbed at 300 °C with a flow path of 200 °C was compared with that from three Tenax TA tubes loaded with the same mix and desorbed at 280 °C with a flow path of 210 °C. The mean % carry-over values obtained for each of these conditions are shown in Table C-12. A higher flow path temperature might be expected to reduce the carry-over in the system and for these compounds equal or lower carry-over was indeed observed in the system using a flow path of 210 °C than found at 200 °C. Again no greater carry-over on the tube was observed using a desorption temperature of 280 °C rather than 300 °C. Therefore, in order to minimise carry-over of SVOCs within the system, a flow path of 210 °C was set for analyses undertaken during the project, with a desorption temperature of 280 °C used to minimise the background for benzene.

Table C-12 Comparison of carry-over of compounds in VOC mix 3 using Tenax TA tubes and two different thermal desorption settings

Compound	Mean % carry-over					
	Desorb at 300 °C for 8 min, cold trap high 300 °C for 3 min, flow path at 200 °C (n = 3)			Desorb at 280 °C for 8 min, cold trap high 300 °C for 3 min, flow path at 210 °C (n = 3)		
	In system	On tube	Total	In system	On tube	Total
Ethyl acrylate	ND	ND	ND	ND	ND	ND
DMF	ND	ND	ND	ND	ND	ND
2-Butoxyethyl acetate	ND	ND	ND	ND	ND	ND
BHA	ND	ND	ND	ND	ND	ND
Diethyl phthalate	0.3	0.1	0.4	0.2	0.1	0.3
TXIB	0.3	0.1	0.4	0.2	0.1	0.3
Dibutyl phthalate	0.2	0.1	0.3	0.2	0.1	0.3
DEHP	0.8	0.1	0.9	0.4	0.1	0.5

C.1.5 Re-collection

The TD-100 is fitted with the facility to allow quantitative and automatic re-collection of the outlet split flow either onto the same or a different sorbent tube thus allowing repeat analysis. This facility was investigated by spiking a conditioned Tenax TA tube with 1 µl of a standard mix containing approximately 1,000 ng of seven compounds in methanol and purging for 5 minutes. The tube was analysed using an outlet split flow of 20 ml min^{-1} (to give a split ratio of 14.3:1) and the split flow re-collected onto a second conditioned Tenax TA tube. The re-collected tube was analysed using the same conditions and its split flow re-collected onto a further tube. This step was repeated followed by analysis of the third re-collection tube. Figure C-4 shows the responses for the seven compounds from the standard mix which had been analysed four times using the re-collection facility. This shows an expected reduction in instrument response for each re-collection as for each step a fraction is sent down the GC column and the remainder re-collected onto a sorbent tube. The facility is therefore shown to have the potential to be of benefit when for some reason it is necessary to re-run a particular sample, for example in the case of instrument failure during a run. This is particularly useful where no duplicate sample is available.

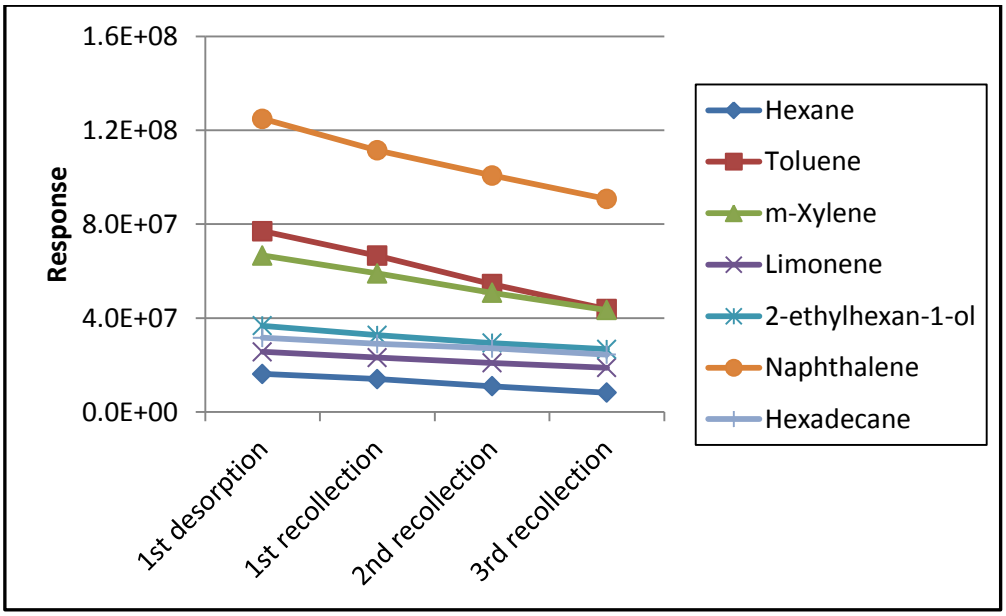

Figure C-4 Responses for seven VOCs using the re-collection facility of the TD-100/GC/MSD system

Following this test, the instrument was set to re-collect the split flow during analysis of samples from material emissions tests. One instance of the re-collected tube being required occurred during the analysis of one sample from a µ-CTE test. This was because the output from the first desorption was passing through the GC column at the time that a filament failed. The re-collection facility also proved of benefit for re-analysing samples from emissions tests of wall covering materials where in the first analysis one or more compounds occurred above their upper limit of quantification (i.e. the point at which the calibration curve becomes non-linear). In this case analysis of the re-collected tube was undertaken using a bigger split ratio so that the amount of the substance reaching the detector is reduced to a quantifiable level. One issue which has been observed with the use of re-collected tubes, however (see Appendix B.1), is a higher benzene background level. A small amount of benzene is produced on each desorption of a tube, thought to be resulting from degradation of the Tenax TA or impurities present in the sorbent, and the extra heating involved in desorbing the tube for a second time results in a greater amount of this compound. Further tests would be required to define the limitations this phenomenon places on the use of a re-collected tube containing Tenax to determine benzene.

C.2 GC settings

C.2.1 Column

One important parameter is the GC column. For indoor air quality monitoring/ material emissions typically a capillary column of length 30 m to 60 m, internal diameter 0.25 mm to 0.32 mm and phase thickness of 0.25 µm to 0.5 µm is used (ISO 16000-6:2011). Appendix D to the standard states that, if VVOCs are of interest, thicker film and/or longer capillary columns may be required. The standard also suggests the use of a non-polar stationary phase, i.e. 100 % dimethylpolysiloxane. Initial work employed a 15 m ZB-5 column of internal diameter 0.25 mm and film thickness 0.25 µm as this was to hand, while advice was sort on a suitable column to investigate. It was decided to acquire and test a 60 m DB-5 (95 % dimethylpolysiloxane, 5 % phenyl methylpolysiloxane) column of internal diameter 0.25 mm and film thickness 0.5 µm.

C.2.2 Temperature programme

ISO 16000-6 (2011) states that "temperature programming of the analytical column is needed when analysing mixtures of substances showing large differences in boiling points and polarities in order to achieve a good resolution in minimal time". A typical GC programme for general VOC analysis runs from 50 to 250 °C at 5 or 10 °C min^{-1}, with an initial hold time of 5 or 10 min at 45 °C and a final hold time of 5 or 10 minutes at 250 °C (Markes, 2005). In order to develop a suitable temperature programme for this project, the separation of the indoor air standard mix was investigated using a range of initial and final temperatures, ramp rates and hold times. This mix contains 50 compounds with boiling points between 40 and 285 °C. Additionally separation of a mixture of higher boiling compounds was investigated in order to optimise the later part of the temperature programme.

The initial temperature program trialled was 5 minutes at 40 °C followed by 2 °C min^{-1} to 75 °C then 5 °C min^{1} to 250 °C at a flow rate of 1.3 ml min^{-1} (run time 62.5 minutes). The chromatogram obtained from analysis, using these conditions, of a dilution of the indoor air standard mix containing approximately 100 ng of each of 50 compounds is shown in Figure C-5. There were five areas of the chromatogram (around 5, 9, 12, 19 and 30 minutes) where peaks were poorly resolved.

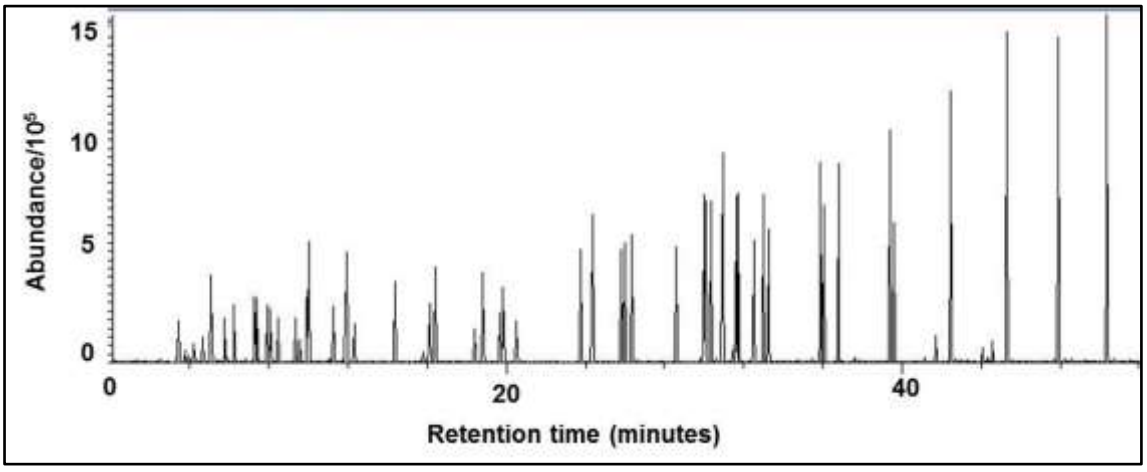

Figure C-5 Chromatogram obtained from analysis of 50 compound mix on the TD-100/GC/MSD system

The retention times of these compounds and those for the first and last eluting peaks in the mix (ethanol and n-hexadecane respectively) are shown in Table C-13, Run A. This mix of compounds was then analysed a further six times with varying temperature programs and flow rates and retention times obtained are also shown in the table (Runs B-G). Run G starting at 35 °C with a 1 minute hold followed by 2 °C min^{-1} to 75 °C then 5 °C min^{-1} to 250 °C (run time 61 minutes) was found to give the best separation.

As the intention is to analyse significantly higher boiling compounds than n-hexadecane, it was decided to raise the final column temperature to 300 °C, increasing the ramp rate to 10 °C min^{-1} from 140 °C in order to avoid an excessively long run. With a final hold time of 12 minutes this would result in a run time of 62 minutes. The 50 compound mixture was analysed using these conditions and good separation was still achieved for the later eluting compounds in the mix. The separation of the three VOC mixes used for the TD desorption experiments was also investigated and good separation was obtained for all peaks. The retention time for the highest boiling compound tested, DEHP, was 54.90 minutes. As this compound has a boiling point of 384 °C, which is likely to be towards the top of the range of compounds which are able to be released by thermal desorption from Tenax TA, a run time of 62 minutes was felt to be sufficient.

C.2.3 Column flow

The instrument is fitted with electronic pneumatic control (EPC) of the carrier gas, so has the option of being operated in either constant pressure or constant flow modes. In constant flow mode the pressure is increased as the GC oven temperature increases during a temperature programmed run so that the flow of helium through the column remains constant which results in sharper peaks throughout the chromatogram. For helium carrier gas the optimum velocity is between 20 and 40 cm sec^{-1}, which is equivalent to a flow rate of between about 1 and 2 ml min^{-1} for a 60 m column of internal diameter 0.25 mm. A higher flow rate, within the optimum range, will result in faster analyses, but this may be limited by the pressure the system is able to supply to maintain the flow at high column temperatures. For this project a constant flow of 1.3 ml min^{-1} was selected, this requires a pressure of around 20 psi at a temperature of 40 °C and around 40 psi for a temperature of 280 °C.

Table C-13 Retention times for compounds from indoor air mix using a range of GC conditions

Compound	Retention Time (minutes)						
	Run A 1.3 ml/min, 5 min @ 40 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C	**Run B 1.4 ml/min, 1 min @ 40 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**	**Run C 1.2 ml/min, 1 min @ 40 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**	**Run D 1.4 ml/min, 5 min @ 40 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**	**Run E 1.3 ml/min, 2 min @ 35 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**	**Run F 1.3 ml/min, 5 min @ 35 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**	**Run G 1.3 ml/min, 1 min @ 35 °C, 2 °C/min to 75 °C then 5 °C/min to 250 °C**
Ethanol	4.64	4.40	4.74	4.47	4.75	4.81	4.70
Acetone	5.06	4.76	5.13	4.88	5.20	5.29	5.14
Propan-2-ol	5.09	4.78	5.15	4.91	5.24	5.34	5.17
Butan-1-ol	9.92	8.61	9.18	9.61	10.13	11.05	9.78
Benzene	9.99	8.75	9.33	9.69	10.20	11.05	9.87
1,2-Dichloropropane	11.86	10.23	10.86	11.51	12.00	13.15	11.60
n-Heptane	11.93	10.25	10.88	11.59	12.09	13.27	11.65
Trichloroethylene	11.96	10.29	10.95	11.61	12.09	13.27	11.70
Tetrachloroethylene	19.66	16.78	17.62	19.23	19.59	21.61	18.90
Butyl acetate	19.85	16.80	17.68	19.43	19.75	21.89	19.02
Mesitylene	30.93	26.89	27.56	30.59	30.52	33.36	29.55
β-Pinene	30.93	26.89	27.56	30.62	30.52	33.36	29.57
n-Hexadecane	50.36	46.08	46.66	50.09	49.86	52.86	48.86

C.3 MSD settings

C.3.1 Scan range

No guidance is given in ISO 16000-6:2011 about the scan range to be used for the determination of VOCs. A typical scan range for such analyses is m/z 35-350, for example, the method described for the California Specification 01350 (Cal01350) (CDPH, 2010) (see Section 1.3.3.2) requires the MS to be operated over 'at least' this range. The 5973 MSD has a maximum scan range of m/z 1.60 to 800, but a large scan range gives a low number of scans/second. This can result in reduced performance if there are insufficient scans across each peak. As compounds outside the VOC volatility range, including smaller and larger molecules than those within the range are of interest in this project, a scan range of m/z 20-450 was applied, resulting in 6 scans per second. A typical peak width for this method is 3 seconds, giving about 18 scans across a peak which is within the range of 15-20 recommended for quantitative analysis (Agilent Technologies, 2005).

C.3.2 Tune type

The MSD is tuned using the compound PFTBA (perfluorotributylamine). This is used as it is stable, volatile and fragments over a wide mass range. The instrument was tuned following instrument maintenance, such as installation of a new column, or after a drop in instrument response. The 5973 offers several different tunes including standard spectra tune, or stune and autotune or atune. ISO 16000-6:2011 recommends the use of 'stune' if using the MS for quantification. This tune gives a standard response over the entire scan range (Agilent Technologies, 2005). 'stune' was used for the bulk of the project, with a comparison of sensitivity obtained with that of 'atune', which maximises instrument sensitivity across the entire scan range, also being undertaken.

C.3.3 Scan type

The modes of ionisation possible on the MSD system available were scan and selected ion monitoring (SIM). SIM allows detection of compounds of interest with very high sensitivity. This is achieved by the instrument collecting data at specific masses, rather than scanning across the whole mass range (Agilent Technologies, 2005). However,

only those compounds which contain the particular ions selected will be detected. Scan mode is therefore required when the compounds present in a sample are not known in advance. Synchronous SIM-scan was not possible on the system available, though the possibility existed to analyse a sample in scan mode with re-collection of the split flow, followed by analysis of the split effluent using SIM mode.

In order to investigate the possibility of increasing the sensitivity of the method by the use of the SIM mode, three replicates of a mixture containing approximately 250 ng of each of the check standard compounds were analysed using scan mode and a further three repeats of the same mixture were analysed using SIM mode. The same target ion was used for each compound in the two modes. Mean peak areas obtained for each compound using these two modes are shown in Table C-14. Peak areas obtained using the SIM mode were between 2.2 and 3.6 times higher than those obtained using scan mode. This suggests that the SIM mode would result in a significant increase in sensitivity if required for particular compounds. However, as well as peak size, signal to noise ratio is of importance to sensitivity and this is investigated during the study of limits of quantification (see Section C.4.1).

Table C-14 Comparison of response using SIM and scan modes to analyse 250 ng of check standard solution

Compound	Target ion	Mean peak area		Ratio of SIM/scan areas
		Full scan mode (n = 3)	SIM mode (n = 3)	
n-Hexane	57	7,115,891	15,672,228	2.2
Methyl isobutyl ketone (MIBK)	43	13,509,468	33,805,642	2.5
Toluene	91	19,389,176	42,227,983	2.2
Hexanal	56	5,183,439	12,274,801	2.4
Butyl acetate	43	16,597,302	42,116,403	2.5
Cyclohexanone	55	10,493,523	24,980,320	2.4
Phenol	94	9,797,571	24,781,018	2.5
1,2,3-Trimethylbenzene (123-TMB)	105	18,712,998	46,578,247	2.5
4-Phenycyclohexene (4-PCH)	104	30,463,005	76,916,701	2.5
Butylated hydroxytoluene (BHT)	205	10,287,308	36,894,519	3.6
n-Hexadecane	57	16,797,049	38,777,143	2.3

C.4 Performance of TD-100/GC/MSD system

C.4.1 Limits of quantification

The most generally accepted qualitative definition of the limit of detection (LOD) of an analytical method is that it is the "minimum amount of analyte that can be detected at a known confidence level. This limit depends upon the ratio of the magnitude of the analytical signal to the size of the statistical fluctuations in the blank signal" (Skoog, 1985). Therefore, certain detection of the analytical signal is only possible if it is larger by some multiple than the variations in the blank. LOD has also been defined as being the "lowest concentration of the component in a sample which can be detected but not necessarily quantified", while the lowest concentration of the component in a sample which can be quantified is defined as the lower limit of quantification (LOQ) (Clausen and Kofoed-Sorensen, 2009). LOQ is often defined as the "analyte mass that produces a response that is 10 times higher than the instrument noise level or is 10 times the standard deviation for repeated analyses of a low level standard" (CDPH, 2010), while LOD can be estimated as "three times the standard deviation of the analysis of 20 low standards" (Clausen and Kofoed-Sorensen, 2009). For this project 20 conditioned Tenax TA tubes were analysed in order to determine the LOQ of compounds occurring in a blank sample, then, during calibration, replicate tubes spiked with low levels of standard solutions were analysed to determine these values for specific compounds contained within the standard mixes.

The upper limit of quantification was determined from the calibration curve for each compound calibrated. This was the point above which the curve became non-linear. For most compounds this was in the range 300-1000 ng and the actual values found are shown in Appendix F.2. Quantification above this level using a curve is a possibility, but was felt to be less satisfactory. The lower limit of quantification (LOQ) for benzene was obtained from the analysis of 20 conditioned Tenax TA tubes using two desorption temperatures (Table C-15). Whilst use of 300 °C results in a LOQ for benzene of 25.7 ng on the tube which, for a 5 litre air sample, would be equivalent to a concentration in the air of 5.1 µg m^{-3}, the use of a temperature of 280 °C results in a LOQ equivalent to a concentration of 1.1 µg m^{-3} for a 5 litre air sample. The lower

desorption temperature therefore provides a significant benefit for the determination of this compound.

Table C-15 Analysis of 20 conditioned Tenax TA tubes to determine LOQ for benzene

Desorption temperature (°C)	78 ion peak area		LOQ (ng)
	Mean	10 x SD	
300	2,474,739	3,565,006	25.7
280	1,079,845	2,358,420	5.3

The results obtained from analysis of five replicate tubes spiked with low levels of VOC mix 3 are shown in Table C-16. The standard solution containing approximately 3 ng of each component was used for most compounds, except for those which were not detectable at this level, where five repeats of the 30 ng level were used. Four of these compounds were found to have a lower limit of quantification of <2 ng on the tube, whilst that for some compounds was slightly higher and that for dimethylformamide (DMF) significantly higher at 34.1 ng. It is not unexpected for the LOQ of different compounds to vary and in particular for compounds with polarity to have higher LOQs on the column used.

Table C-16 Determination of LOQ for compounds in VOC mix 3

Compound	Amount spiked (ng)	Extracted ion peak area (n = 5)		LOQ (ng)
		Mean	10 x SD	
Ethyl acrylate	3	125,699	157,528	3.0
DMF	30	450,176	461,403	34.1
2-Butoxyethyl acetate	3	117,333	80,114	3.4
BHA	3	145,326	76,691	1.2
Diethyl phthalate	4	425,381	239,967	1.6
TXIB	3	517,440	332,891	1.7
Dibutyl phthalate	4	980,322	469,034	0.6
DEHP	30	3,528,238	2,601,395	9.9

For the 11 compounds contained in the check standard solution, a more thorough determination of LOQ was undertaken by analysing 20 replicate tubes spiked with approximately 2.5 ng of each compound. LOQ values calculated from all 20 analyses

and root mean square (RMS) signal to noise (S/N) values calculated within ChemStation from one of the files are shown in Table C-17. Most of these compounds were found to have a lower limit of quantification of around 1-2 ng on the tube, whilst that for hexanal was found to be 6.7 ng and that for phenol was 21.5 ng. For the other compounds for which calibrations have been undertaken the LOQ was estimated from a study of the responses obtained from analysis of the duplicate low level standards during calibration.

Table C-17 Determination of LOQ for check standard compounds using full scan

Compound	Extracted ion peak area (n = 20)		Signal to noise (S/N) (n = 1)	LOQ (ng)
	Mean	%RSD		
n-Hexane	82,730	9.0	93	1.6
MIBK	131,582	6.6	38	1.6
Toluene	259,549	6.6	285	1.4
Hexanal	78,270	17.2	63	6.7
Butyl acetate	152,812	7.7	40	2.2
Cyclohexanone	105,632	5.2	81	1.6
Phenol	251,676	31.6	607	21.5
1,2,3-TMB	178,355	5.9	479	1.4
4-PCH	318,864	4.0	1,022	1.1
BHT	115,934	8.0	651	2.5
n-Hexadecane	200,399	8.0	281	2.0

ISO 16000-6:2011 does not make specific mention of the required LOQ for analysis of VOCs in chamber air, however it does state that "as many compounds as possible should be analysed and particularly those present at concentrations above 2 µg m^{-3}" (BS ISO 16000-6, 2011). The AgBB scheme states that "the identification of all individual substances is based on a presumed uniform detection limit of 1 µg m^{-3} in order to cover the emission spectrum as fully as possible" (AgBB, 2012). Cal01350 states that "the lower LOQ for VOCs appearing on the list of chemicals of concern and for non-listed VOCs should be 2 µg m^{-3} or better" (CDPH, 2010). It also states that "a lower LOQ that is higher than the absolute value, obtained from repeated injection of low level standards, may be defined based on practical considerations". For a 5 litre sample of air, a LOQ of 5 ng on the tube is equivalent to a concentration of 1 µg m^{-3}. Therefore, the

majority of compounds investigated have been found to have an acceptable LOQ, the exception being some polar compounds for which such an observation has been made previously (Horn et al., 2007). For reporting purposes, it was decided to set a minimum LOQ of 5 ng for those compounds where a value of ≤5 ng had been obtained. Resulting LOQ values for all compounds for which full calibration was undertaken are given in Appendix F.2

Two experiments were undertaken to investigate the potential for improving LOQ values if this is required, namely the use of SIM rather than full scan mode and the use of autotune rather than standard spectra tune. The results obtained from analysis of a further five replicates of the 2.5 ng level of the check standard solution, using the SIM mode, Table C-18, show significantly larger mean peak areas than found using scan mode. This is consistent with the findings of the preliminary investigation of the use of SIM in Section C.3.3. An approximate calculation of LOQ from this data (using the full scan calibration factors for these compounds) suggests that most of them would be quantifiable at <1 ng with phenol at <10 ng. So the use of SIM mode would give a reduced LOQ for these compounds if this was required. (No S/N values obtained from this data as no noise was measurable using the ChemStation S/N tool).

Table C-18 Investigation of use of SIM for determination of check standard compounds

Compound	Selected ion peak area (n = 5)		Approximate LOQ (ng)
	Mean	%RSD	
n-Hexane	189,883	3.3	0.1
MIBK	329,789	1.7	0.2
Toluene	539,849	4.2	0.1
Hexanal	181,256	10.4	3.4
Butyl acetate	412,214	2.5	0.6
Cyclohexanone	261,591	4.7	1.4
Phenol	601,986	13.7	9.1
1,2,3-TMB	440,927	2.1	0.3
4-PCH	765,697	2.0	0.5
BHT	423,035	4.4	2.1
n-Hexadecane	444,264	2.6	0.2

The results obtained from the use of autotune rather than standard spectra tune (stune), are shown in Table C-19. These values, which are again obtained from five replicate analyses of a solution containing approximately 2.5 ng of the check solution compounds, show larger mean peak areas for some of the compounds and smaller areas for others compared with use of stune (Table C-17). This is not unexpected as each compound uses a different ion for quantification and the two tunes optimise sensitivity differently across the scan range. A comparison of the S/N values obtained using the two tunes shows slightly higher values for most of the compounds using atune, except for hexanal and cyclohexanone for which stune gave a higher value. Calibration for these compounds using atune would be required to calculate LOQ values for this setting, but these results suggest that use of autotune may result in enhancement in sensitivity for some of the compounds.

Table C-19 Investigation of use of full scan and autotune for determination of check standard compounds

Compound	Extracted ion peak area (n = 5)		S/N (n = 1)
	Mean	%RSD	
n-Hexane	77,243	8.3	148
MIBK	104,326	4.9	56
Toluene	425,824	3.5	299
Hexanal	50,638	19.4	36
Butyl acetate	116,550	8.2	69
Cyclohexanone	93,368	9.3	55
Phenol	371,024	40.0	816
1,2,3-TMB	312,881	4.6	660
4-PCH	526,139	4.0	2,400
BHT	613,807	17.8	3,456
n-Hexadecane	178,136	6.0	313

C.4.2 Quality control

A mixture of seven VOCs, each at an approximate concentration of 80 ng μl^{-1} in methanol, was prepared to act as the quality control (QC) solution at the start of the project. The compounds contained in the mixture were n-hexane, toluene, m-xylene, limonene, 2-ethylhexan-1-ol, naphthalene and n-hexadecane and these were selected to cover the VOC volatility range and include some different compound types. This solution was used for the repeatability tests undertaken during development of the method and then injected daily before analysis of a batch of samples during the first year of the project in order to check the performance of the instrument.

The results obtained from all analyses of the seven compound mix were entered into a spreadsheet in order to monitor the performance of the instrument over time. A plot of normalised response (peak area per ng of component) obtained for two of the compounds (toluene and naphthalene) is shown in Figure C-6. A large variation in response for both compounds is observed during April-May 2010, this was the period after the switching of the mass flow controllers when poor repeatability was eventually rectified by re-setting the needle valve (as discussed in Section 0). Good repeatability was obtained from this time onwards up until the end of this phase of the project.

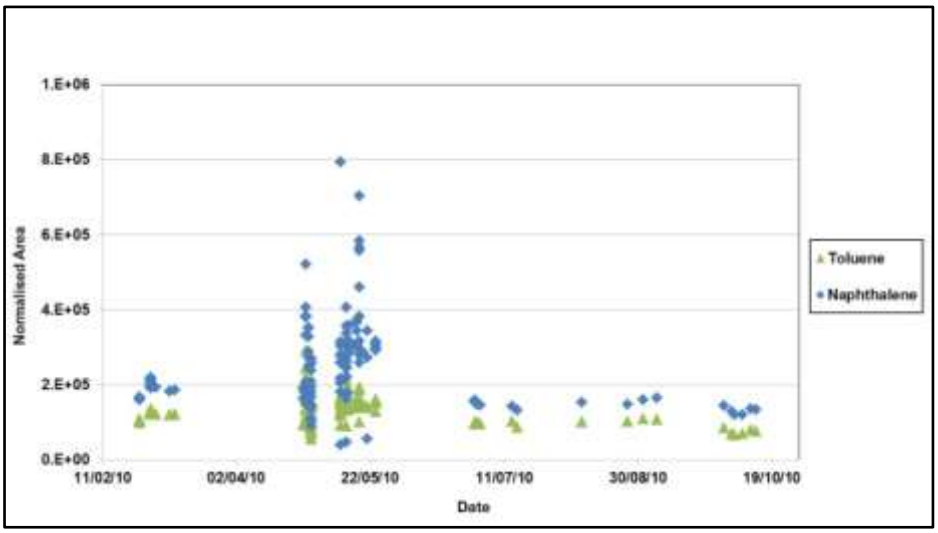

Figure C-6 Normalised response for two VOCs in the QC solution used to test the performance of the TD-100/GC/MSD system during the first year of the project

A calibration for the seven QC mix compounds undertaken in July 2010 enabled the % recovery (amount obtained/amount loaded x 100) for each compound in subsequent analyses of the QC solution to be calculated. Results obtained for toluene and naphthalene are shown in Figure C-7 and Figure C-8 respectively. These figures also show warning levels (in green) set at ±2 SD from the mean recovery and action levels (in red) set at ±3 SD from the mean. If a value exceeding the action level is obtained the performance of the instrument should be investigated.

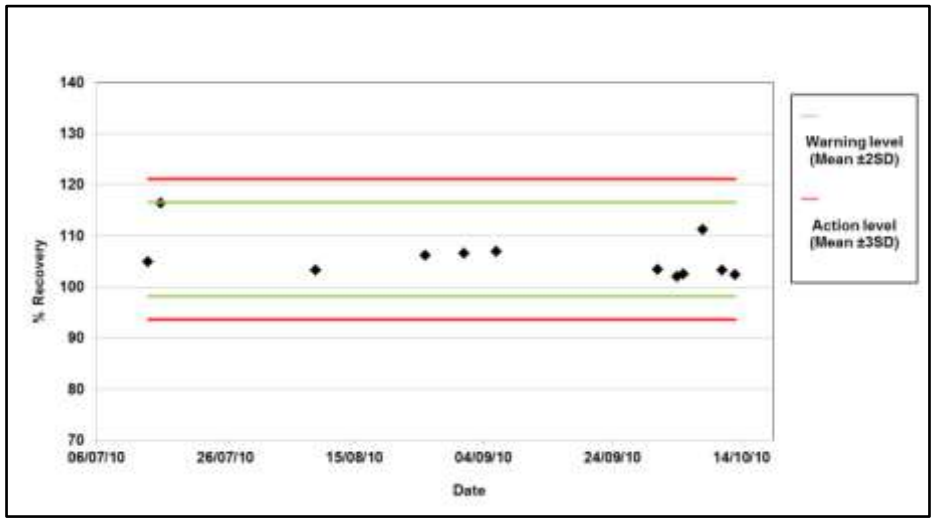

Figure C-7 Percentage recovery for toluene in the initial QC solution used to monitor performance of the TD-100/GC/MSD system

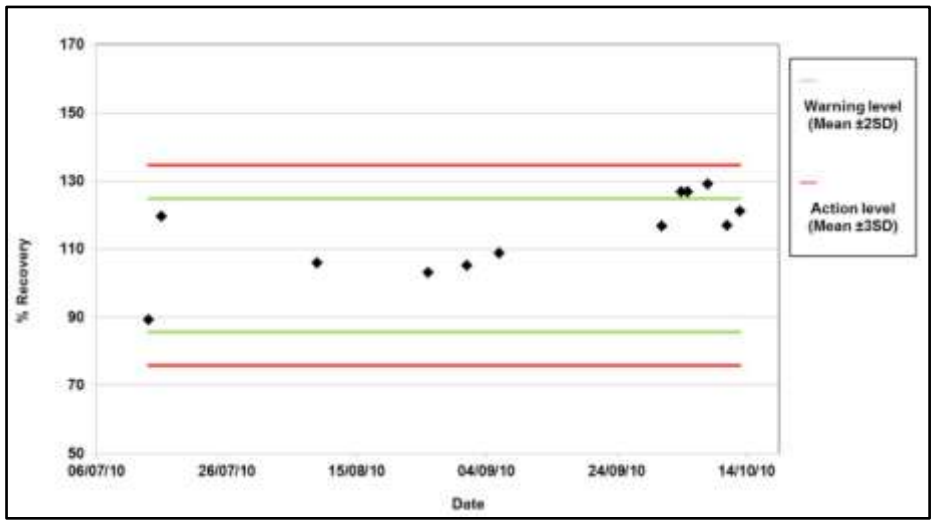

Figure C-8 Percentage recovery for naphthalene in the initial QC solution used to monitor performance of the TD-100/GC/MSD system

Good recovery was obtained over the period for both compounds, with the mean recovery for toluene being 107.4 % (RSD 4.3 %) and that for naphthalene being 105.3 % (RSD 9.3 %). The recovery for naphthalene showed an increase towards the end of the period showing that re-calibration with a freshly prepared mixture was required. At this time, however, the 11 compound 'check standard' mix (see Section 1.4.1) became the QC solution for monitoring the performance of the analytical system.

The first solutions containing the 11 check standard compounds were prepared in October 2010 and a full calibration was undertaken with this mixture. A chromatogram of the check standard solution is shown in Figure C-9. Good peak shapes were obtained for all compounds, with the exception of phenol (retention time 29.17 minutes) which gave a tailing peak with a second smaller peak after it. This compound is highly polar and is therefore expected to be the most difficult of the check standard compounds to analyse on a DB-5 column. Results obtained from regular analysis of a mid-range standard (approximately 80-100 ng of each component), in advance of analysis of a batch of samples, were monitored. An independently prepared check standard solution containing the 11 compounds in dichloromethane was also acquired and was used to check the accuracy of the in-house prepared standard solution. This mixture was commercially produced by ChemService laboratories, West Chester, PA, USA and was supplied in a sealed vial containing 1 ml of solution with each component present at a reported concentration of 100 µg ml^{-1}.

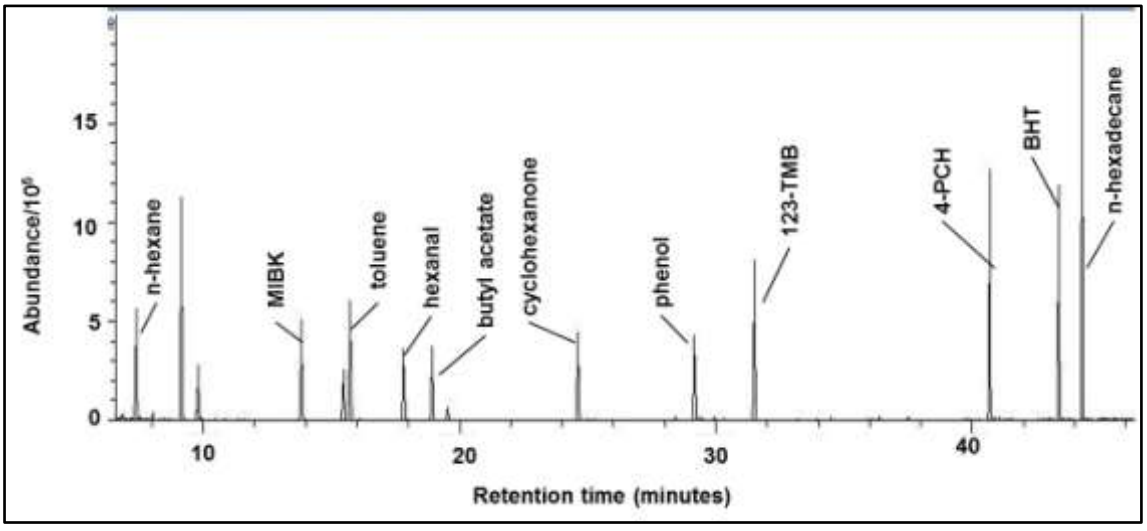

Figure C-9 Chromatogram obtained from analysis of check standard solution

Normalised responses obtained for the internal standard (d8-toluene) and for two of the components (toluene and 4-phenylcyclohexne [4-PCH]) are shown in Figure C-10. This shows the importance of including an internal standard when using mass spectrometry for calibration, as the variation in response for d8-toluene is observed to track fairly well that of the two analytes. No obvious trends in the responses are observed over this period, however, suggesting that there has been no decline in the sensitivity of the instrument.

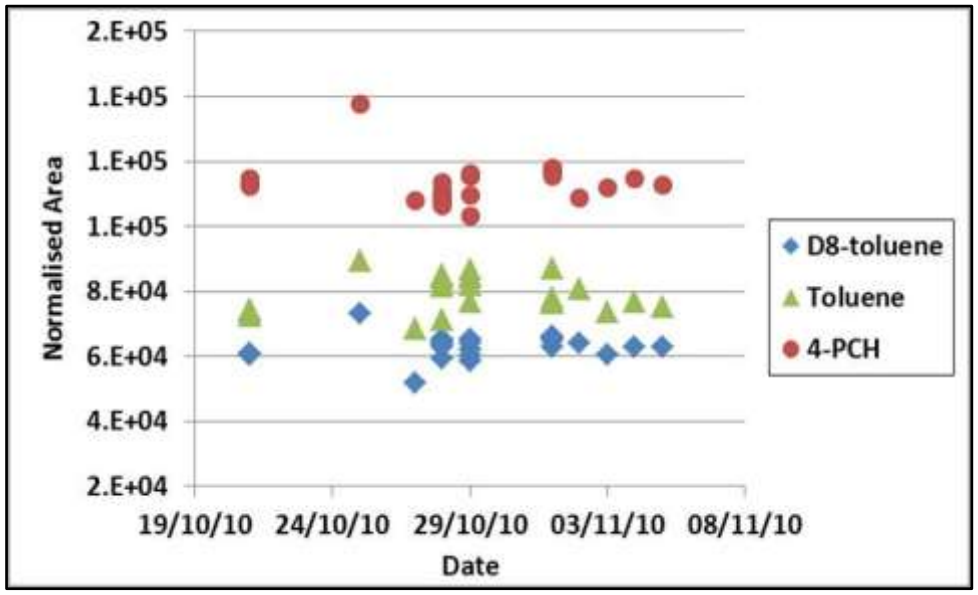

Figure C-10 Normalised response for internal standard and two components of check standard solution

Percentage recoveries obtained for toluene and 4-PCH against their respective calibration curves are shown in Figure C-11 and Figure C-12 respectively. These figures are separated into values obtained from analysis of the in-house prepared standard solution and those from analysis of the independently prepared solution. Percentage recoveries of between 109.7 and 131.0 % for both solutions combined were obtained for toluene with a mean of 118.8 % (RSD 5.7 %) and between 96.1 and 121.8 % for 4-PCH with a mean of 105.5 % (RSD 4.7 %). Similar results were obtained for the other compounds, with mean recoveries, for both solutions combined, of 102.8 to 121.7 %. The mean recovery for phenol (106.3 %) was better than might have been expected given the poor peak shape obtained for this compound.

For toluene, the independently prepared solution gave a slightly higher recovery (mean of 124.9 % after 12 analyses) than that obtained after 14 analyses of the in-house solution (113.5 %) and this difference was found to be statistically significant (t-test, 95 % confidence). For 4-PCH a closer result is seen, with the mean value obtained using the independently prepared solution (103.1 %) being significantly lower than that obtained for the in-house solution (107.6 %). A similar small bias between the two solutions was observed for MIBK, cyclohexanone and 1,2,3-trimethylbenzene, which all gave a significantly higher mean recovery for the independently prepared solution than for the in-house solution, and for hexanal, butyl acetate and BHT, which all gave a significantly lower value for this solution, but no such bias was observed for n-hexane, phenol or n-hexadecane. Therefore, no systematic difference is emerging in the preparation of standard solutions between the two laboratories.

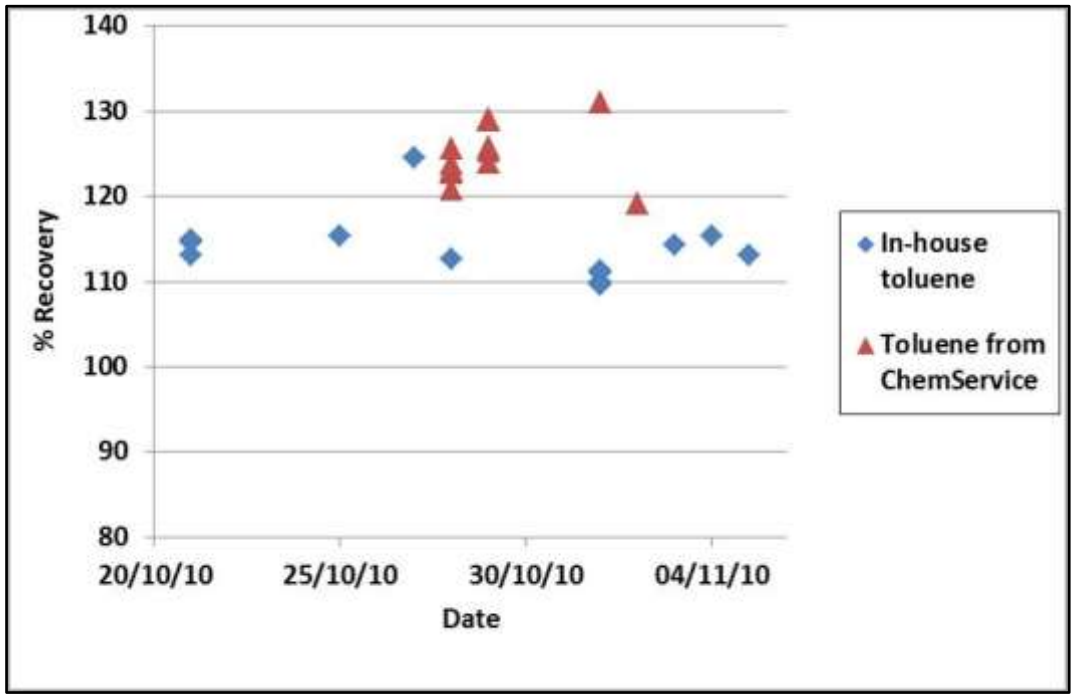

Figure C-11 Percentage recovery for toluene in in-house and independently prepared check standard solutions

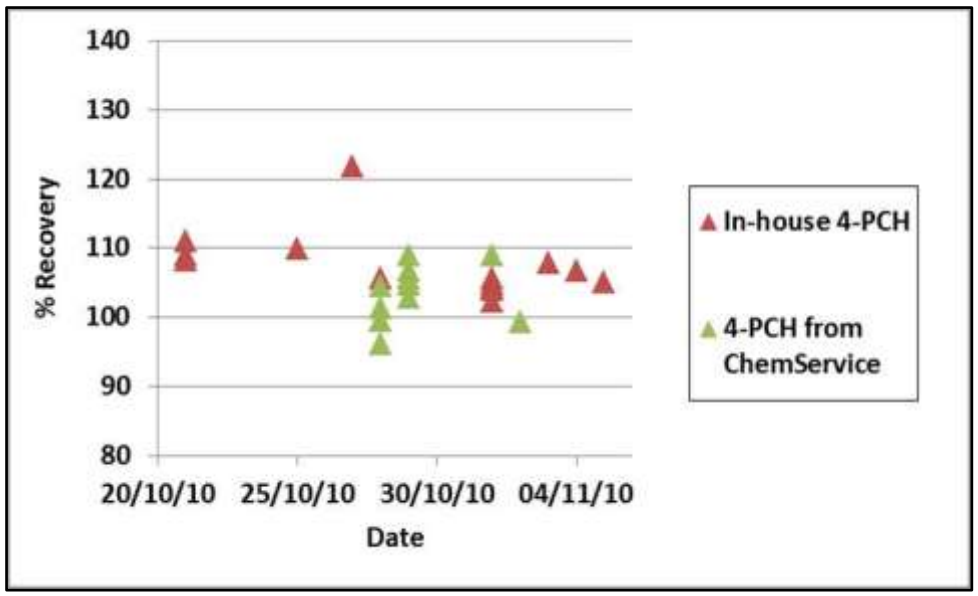

Figure C-12 Percentage recovery for 4-PCH in in-house and independently prepared check standard solution

Monitoring of the performance of the analytical system continued through daily analysis of the 11 compound check standard solution during periods of operation, with preparation of new standard solutions and further multi-level calibrations of the system being undertaken as required. A QC chart showing the % recovery obtained for toluene and 4-PCH over the period March to October 2011 is shown in Figure C-13. The majority of the results obtained are between 95 and 120 % and there seems to be a tendency for values for both compounds to gradually increase with time until brought on track by either re-tuning or re-calibrating the instrument. One anomalous low value for 4-PCH was observed in July and there were two incidences where the values increased to >140 %. In each case the recovery was closer to the expected value for subsequent runs. Operation of this QC procedure has therefore provided confidence in the amounts of VOCs determined during analyses as part of this project.

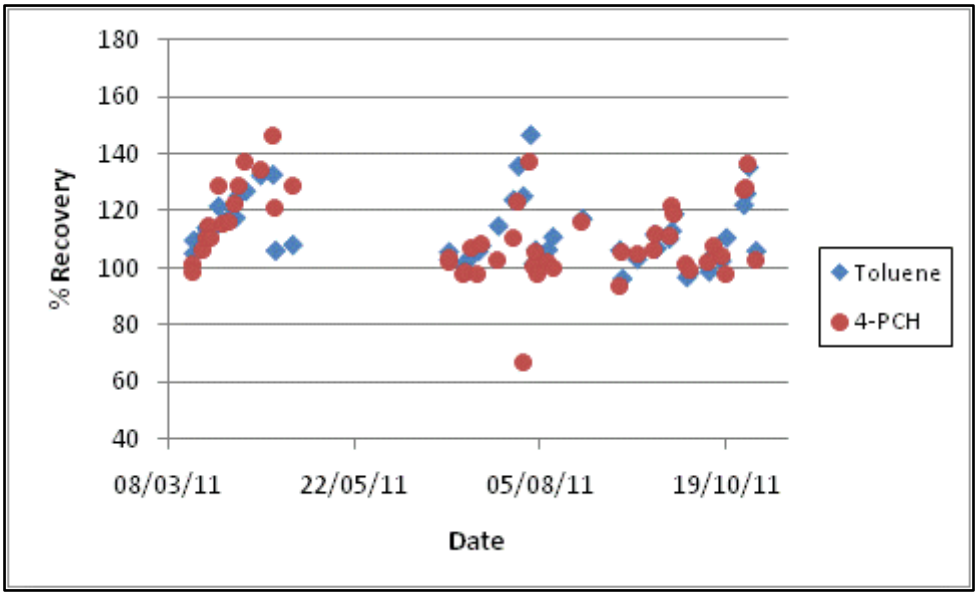

Figure C-13 QC chart to monitor performance of TD-100/GC/MSD system prior to loading each batch of samples analysed during 2011

C.4.3 Quality assurance

Further confidence in the quality of analyses undertaken using the TD-100/GC/MSD system has been gained through participation in two inter-laboratory exercises over the duration of the project. During the first year of the project there was the opportunity to participate in an exercise organised by the National Physical Laboratory (NPL), Teddington as one component of the National Measurement Programme supported by the UK Department of Business, Innovation and Skills. The aim was to establish the accuracy with which emissions testing laboratories are able to test the emissions from a wide range of products emitting VOCs and SVOCs to the atmosphere. For this NPL loaded a batch of tubes containing Tenax TA sorbent with benzene, toluene, o-xylene, butyl acetate, 2-ethylhexan-1-ol and dodecane at levels, known to them, of between 100 and 300 ng. Four loaded tubes were sent to each participating laboratory during July 2010, together with one tube which had not been loaded with analytes, to act as a blank. A calibration was undertaken on the TD-100/GC/MSD system for these specific chemicals, then the five tubes were spiked with the internal standard and analysed. Amounts of each of the six components found on the tubes were determined and reported to NPL.

Amounts of each of the six VOCs found on the four loaded tubes supplied by NPL are shown in Table C-20. Good repeatability was found, with the RSD being ≤ 2 % for all compounds. No detectable amounts of any of the compounds were found on the blank tube which accompanied the other tubes. Results were received from NPL during September and these are shown in Table C-21.

Table C-20 Amounts of six VOCs found on loaded tubes supplied by NPL, July 2010

Compound	Amount found (ng)				Mean	%RSD
	Tube 1	Tube 2	Tube 3	Tube 4		
Benzene	175.1	178.8	170.4	173.6	174.5	2.0
Toluene	198.8	200.5	194.3	199.1	198.2	1.4
Butyl acetate	213.9	216.9	207.5	215.0	213.3	1.9
o-Xylene	222.1	226.2	216.8	222.1	221.8	1.7
2-Ethylhexan-1-ol	219.1	219.9	217.4	220.4	219.2	0.6
Dodecane	209.8	212.3	207.7	213.6	210.8	1.3

Table C-21 Amounts of six VOCs loaded by NPL, July 2010, and scoring of IEH results

Compound	Loaded amount (ng)	% Deviation by IEH from loaded amount	Population Standard Deviation	z score for IEH
Benzene	177	-1.4	7.1	0.7
Toluene	189	4.8	4.8	3.3
Butyl acetate	201	6.1	10	1.7
o-Xylene	204	8.7	15	1.4
2-Ethylhexan-1-ol	209	4.9	20	0.9
Dodecane	197	7.0	13	1.5

Deviations from the amounts loaded by NPL were ≤ 9 % for all compounds, with slightly higher values being obtained than the loaded value for all compounds, except for benzene for which a recovery of 1.4 % below the loaded amount was obtained.

NPL received results from 13 laboratories from which they identified seven laboratories to use in the analysis of the results. These laboratories had standard deviations and differences between amounts loaded and amounts found which were compatible in measurement uncertainty to the amount loaded values with their uncertainties. They

used the results obtained by these seven laboratories to calculate population standard deviations for each of the six compounds and then calculated z scores for each result from these. The quantity z represents the difference between the known loaded quantity and the laboratory's analysed result in units of standard deviation for each VOC. Z scores obtained for all laboratories are shown in Figure C-14 and those for laboratories A-G, which were used in the calculation of the z scores, are shown in Figure C-15. In these figures, results obtained by the IEH laboratory are shown as Laboratory B. In conventional statistics a z-score of less than or equal to 2 is statistically acceptable (at a 95 % confidence level) and greater than 3 is not (though this applies strictly to populations that are much larger than here however). Good results were obtained by this laboratory with z scores of <2 for all compounds other than toluene, for which a value of 3.3 was recorded. No explanation was found for the greater error obtained for this compound.

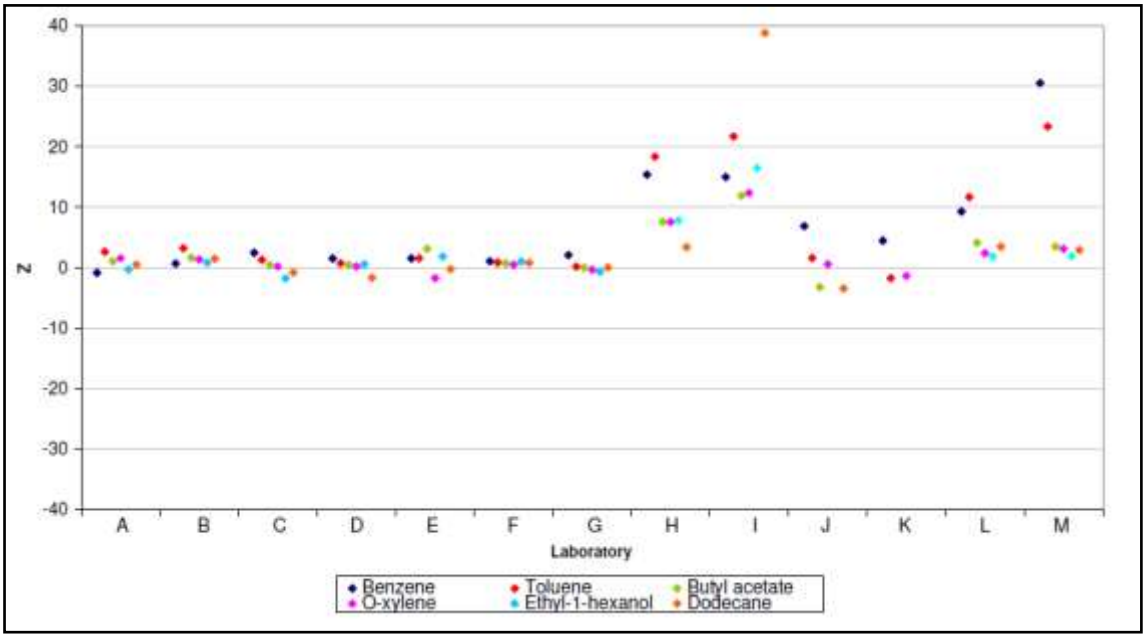

Figure C-14 Z scores obtained for all laboratories participating in NPL inter-laboratory comparison exercise July 2010 (supplied by NPL, 2010)

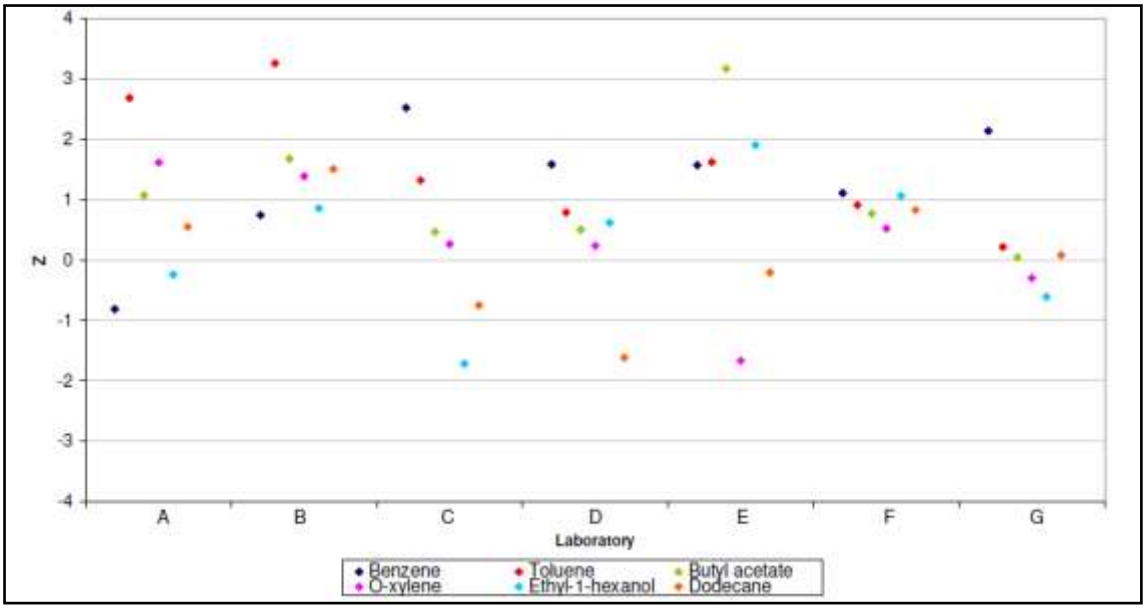

Figure C-15 Z scores obtained by the top seven laboratories participating in NPL inter-laboratory comparison exercise July 2010 (supplied by NPL, 2010)

During the second year of the project, as part of the setting up of a proficiency scheme for material emissions testing (see Section 1.4.3), HSL supplied a set of eight tubes for analysis. These had been loaded with the check standard compounds, together with o-xylene and 3-methylcyclohexanone. These tubes were analysed on the TD-100/GC/MSD system and the results reported to HSL. The loading level of these compounds was not accurately determined; the main purpose of this test being to ascertain the repeatability of the loading procedure and to be advised of any other issues which might come to light. Results of the analysis of this batch of tubes, however, also serve as a check on the repeatability of the analytical system.

The results obtained from analysis of eight tubes at IEH and eight at HSL are shown in Table C-22. The variability for n-hexane was expected to be high as the tubes had been loaded using a purge of 4 litres of air and this may result in the loss of some of this compound from the tube. A similar pattern in the relative standard deviations was observed by the two laboratories with higher values for n-hexane, n-hexadecane and phenol than for the other compounds.

Table C-22 Results obtained for preliminary loading of tubes with check standard mixture at HSL

Compound	%RSD		Approximate loading level (ng)	Amount found by IEH (ng)	% recovery
	HSL	IEH			
n-Hexane	7.3	6.6	87	90	103
4-methylpentan-2-one (MIBK)	1.1	2.6	101	130	129
Toluene	1.6	1.9	167	149	89
Hexanal	2.0	7.4	96	118	123
Butyl acetate	0.9	2.1	90	149	165
Cyclohexanone	0.9	1.9	118	149	126
o-Xylene	1.9	1.6	170	N/C	---
3-Methylcyclohexanone	1.1	1.9	118	N/C	---
Phenol	2.5	5.2	97	N/C	---
1,2,3-Trimethylbenzene (123-TMB)	1.7	1.7	154	138	90
1-Phenylcyclohexene	1.7	2.8	171	N/C	---
BHT	3.5	2.4	180	156	87
n-Hexadecane	5.9	5.0	104	90	87

N/C = no calibration undertaken for this compound

The RSD of 7.4 % obtained by IEH for hexanal however suggested that the performance of the instrument may be starting to deteriorate, and in fact shortly after this time the chromatograms were found to suffer from contamination which was eliminated by the instrument being serviced. An amount found on the tube was only reported for those compounds for which a current calibration curve was available. These values were not expected to necessarily be a good match to the loading levels estimated for the tubes which were determined relative to a single toluene reference standard (i.e. not taking into account the response factors for the different compounds). A reasonable correlation is nevertheless observed for some of the compounds, with greater divergence for others.

The set of tubes loaded by HSL with check standard compounds was followed, during the third year of the project, by a further set of tubes loaded with a similar set of compounds as part of a more formal inter-laboratory trial in advance of the

commencement of the material emissions proficiency testing scheme (Butler et al., 2012). The compounds included in this mix were the 11 check standard compounds, with the removal of hexanal and BHT which had been found not to be stable on storage on the tubes, and with the addition of benzene, o-xylene, α-pinene and limonene. The tubes were dynamically spiked from a gaseous atmosphere as described in Section 4.2.2. Five batches of 29 tubes were consecutively prepared by HSL, all at a target loading in the range 140-160 ng per component. One tube from each batch was dispatched to each of the 20 participating laboratories during January 2012, together with one tube which had not been loaded with analytes, to act as a blank. Three tubes from each batch were analysed at HSL to study the homogeneity of the batches. A calibration was undertaken at IEH for these specific chemicals, then the five tubes were spiked with the internal standard and analysed. Amounts of each of the components found on the five tubes were determined and reported to HSL. Good repeatability was found (Table C-23), with the RSD being ≤ 5 % for all compounds, with the exception of hexadecane for which a value of 21.9 % was obtained. Detectable amounts of just two of the compounds (benzene [10 ng] and phenol [36 ng]) were found on the blank tube which accompanied the other tubes.

Theoretical loading levels for the tubes, together with amounts found for those analysed in the homogeneity study at HSL and deviations from these amounts obtained by IEH, are shown in Table C-24. For all these compounds a fairly close result was obtained between the theoretical loading and the amount found on analysis at HSL. Hexadecane is not included in this table as the amount of this compound was found to vary significantly between the batches. Variation in the loading of hexadecane was also found in the comparison of sorbents study (Section 4.3.2) where the reason was believed to be the involatility of this compound. This explains the high variation in the amount of hexadecane found on the tubes from different batches analysed at IEH. Deviations between the amounts found by IEH and those found by HSL were ≤ 17 % for all compounds, with slightly lower values being obtained by IEH for all compounds, except for n-hexane and phenol for which 7.8 % and 10.4 % more respectively was found by IEH than by HSL.

Table C-23 Amounts of 13 VOCs found on loaded tubes analysed at IEH as part of the material emissions proficiency testing scheme trial round

Compound	Amount found (ng)					Mean	%RSD
	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5		
n-Hexane	164.0	168.1	166.2	166.5	165.3	166.0	0.9
Benzene	143.1	146.3	142.1	148.9	145.5	145.2	1.9
MIBK	136.6	140.5	135.9	140.5	136.6	138.0	1.6
Toluene	144.0	147.0	143.0	149.1	144.8	145.6	1.7
Butyl acetate	137.0	141.2	135.3	144.2	138.3	139.2	2.5
α-Pinene	132.2	133.4	126.7	127.8	119.2	127.9	4.4
o-Xylene	147.0	147.5	146.0	150.7	145.6	147.4	1.4
Cyclohexanone	137.7	139.2	136.9	142.1	136.9	138.6	1.6
Phenol	139.7	147.7	147.0	159.9	145.4	147.9	5.0
123-TMB	136.3	136.9	136.9	138.4	134.4	136.6	1.1
Limonene	127.9	130.9	126.6	127.9	123.1	127.3	2.2
4-Phenylcyclo-hexene (4-PCH)	131.3	130.8	129.5	133.3	127.1	130.4	1.8
Hexadecane	92.3	108.0	113.4	124.2	67.1	101.0	21.9

The results obtained by all participating laboratories for toluene are shown in Figure C-16 and corresponding values for 4-phenylcyclohexene (4-PCH) are shown in Figure C-17. Laboratory number 1 represents HSL determined values following sample production, Laboratory number 8 represents HSL acting as a participant and Laboratory number 13 represents IEH. Results from all the participating laboratories were analysed by HSL using a robust statistical approach (Butler et al., 2012) to generate a robust mean and standard deviation for each compound (also included in Table C-24).

Deviations in the amounts found by IEH from the robust participant mean were between 7 and 18 % for all compounds, except for α-pinene and limonene for each of which the amount found by IEH was 25 % below the robust mean. The reason for the somewhat larger deviation for these two compounds is not explained.

Table C-24 Theoretical loading level of compounds and HSL and participant findings for material emissions proficiency testing scheme trial round (includes data from Butler et al., 2012)

Compound	HSL theoretical target loading (ng)	HSL homogeneity study (ng) (n=15)		% Deviation by IEH from HSL findings	Robust participant mean (ng)		% Deviation by IEH from robust mean
		Mean	% RSD		Mean	% RSD	
n-Hexane	146	154	3.9	7.8	179	29	-7.3
Benzene	151	162	1.9	-10.4	163	20	-10.9
MIBK	150	151	2.6	-8.6	166	15	-16.9
Toluene	149	156	3.2	-6.7	168	16	-13.3
Butyl acetate	148	144	2.8	-3.3	157	13	-11.3
α-Pinene	156	153	1.3	-16.4	167	19	-24.8
o-Xylene	154	158	4.4	-6.7	179	22	-17.7
Cyclohexanone	150	153	3.3	-9.4	170	17	-17.0
Phenol	157	134	11.2	10.4	129	29	14.7
123-TMB	160	145	1.4	-5.8	148	15	-7.7
Limonene	160	145	1.4	-12.2	169	24	-24.7
4-PCH	155	139	0.7	-6.2	155	20	-15.9

The results of this inter-laboratory trial were to be used by HSL to assist in the setting of initial reference values and standard deviations for performance assessment for generation of the required z-scores for subsequent proficiency testing rounds. Options for reference values included theoretical tube loading values, representative samples analysed at HSL and results of participant data using classical and/or robust statistical protocols. A further purpose of the trial was to provide participants with information on how well they have performed against their peers. This purpose has been achieved for the IEH laboratory with evidence being provided that reliable information was continuing to be obtained from the TD-100/GC/MSD system.

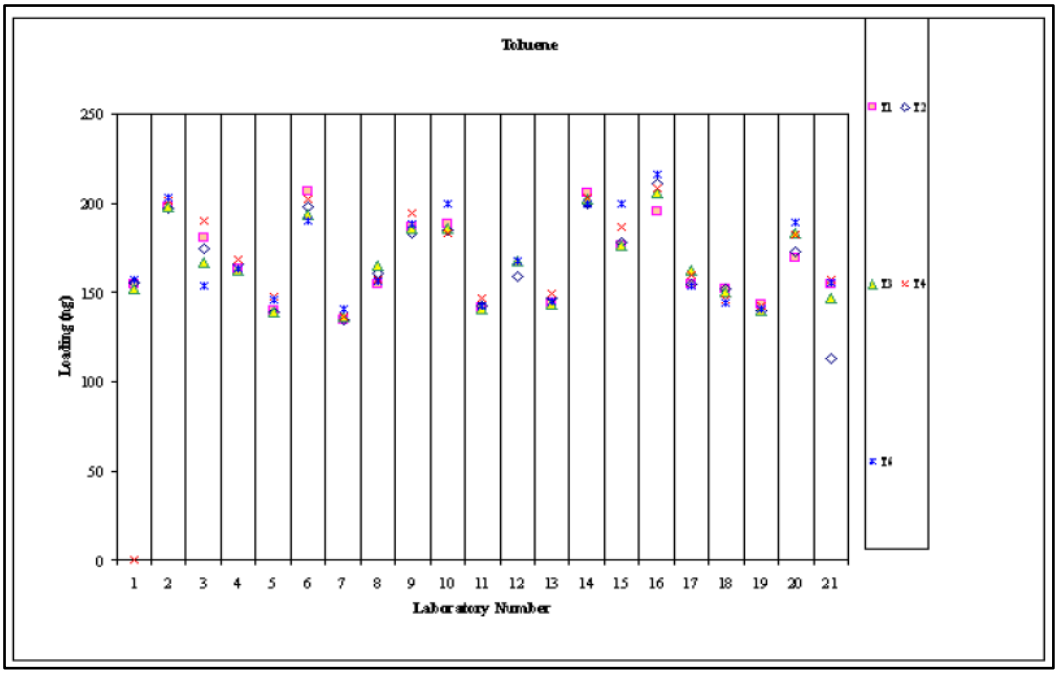

Figure C-16 Results obtained for toluene for all laboratories participating in the material emissions proficiency testing trial round (Butler et al., 2012)

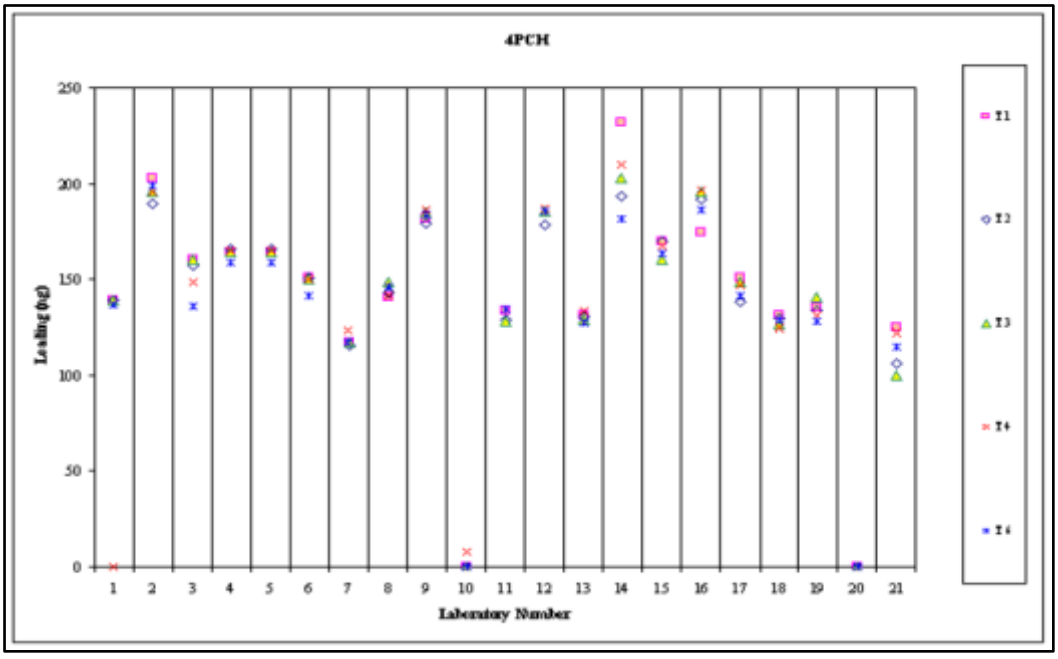

Figure C-17 Results obtained for 4-PCH for all laboratories participating in the material emissions proficiency testing trial round (Butler et al., 2012)

C.4.4 References to Appendix C

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Appendix D Supporting information for Chapter 4

D.1 Full results of emissions tests using μ-CTE and testing with two sorbent types

Table D-1 Dominant compounds emitted from first 15 minute air sample from wall covering 1 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS ¶
	Mean	%RSD	Mean	%RSD			
Toluene	142	16.6	162	11.1	0.3069	1.1702	NS
n-Decane	2,120	11.8	2,150	13.8	0.8998	0.1341	NS
n-Undecane	1,030	11.3	1,020	18.5	0.9414	0.0782	NS
2-Ethylhexanoic acid	339	20.2	468	13.2	0.072	2.4293	NS
n-Dodecane	96.6	9.9	95.1	15.1	0.8876	0.1506	NS
TXIB	3,070	18.0	3,240	6.2	0.6432	0.5002	NS
TVOCs	15,100	12.6	15,300	15.9	0.9161	0.1122	NS

¶ S = significantly different, NS = not significantly different (at the *P* = 0.05 probability level)

Table D-2 Dominant compounds emitted from second 15 minute air sample from wall covering 1 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	76.9	20.9	104	8.7	0.0637	2.5448	NS
n-Decane	1,390	10.6	1,640	9.0	0.1061	2.0794	NS
n-Undecane	740	11.0	848	14.4	0.2718	1.2735	NS
2-Ethylhexanoic acid	450	23.5	527	16.3	0.3827	0.9796	NS
n-Dodecane	73.6	6.0	83.5	15.6	0.2825	1.2408	NS
TXIB	3,190	25.7	3,510	8.4	0.5596	0.6356	NS
TVOCs	9,600	10.0	11,800	6.8	0.0381	3.0479	S

Table D-3 Dominant compounds emitted from first 15 minute air sample from wall covering 1 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	334	11.3	264	39.8	0.3393	1.0840	NS
n-Decane	4,510	17.9	3,900	9.2	0.0435	2.9149	NS
n-Undecane	2,510	21.6	2,240	9.5	0.4659	0.8050	NS
2-Ethylhexanoic acid	2,600	31.4	2,390	12.9	0.6987	0.4161	NS
n-Dodecane	284	23.3	266	7.2	0.6750	0.4515	NS
TXIB	5,900	22.5	5,260	10.0	0.4918	0.7558	NS
TVOCs	44,600	19.0	41,400	10.9	0.5936	0.5790	NS

Table D-4 Dominant compounds emitted from second 15 minute air sample from wall covering 1 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	132	23.1	93.2	52.7	0.3092	1.1637	NS
n-Decane	2,790	18.1	2,540	21.1	0.5881	0.5880	NS
n-Undecane	1,670	21.5	1,590	11.3	0.7595	0.3278	NS
2-Ethylhexanoic acid	2,700	30.9	2,520	9.9	0.7389	0.3574	NS
n-Dodecane	204	22.4	200	9.6	0.8959	0.1394	NS
TXIB	5,810	18.0	5,790	10.7	0.9787	0.0285	NS
TVOCs	26,600	21.9	23,700	13.8	0.4938	0.7522	NS

Table D-5 Dominant compounds emitted from first 15 minute air sample from wall covering 2 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	116	7.5	102	7.1	0.0983	2.1472	NS
n-Decane	442	11.2	426	14.9	0.7476	0.3448	NS
n-Undecane	266	13.1	263	13.2	0.9208	0.1059	NS
2-Ethylhexanoic acid	163	8.1	153	8.7	0.4076	0.9243	NS
n-Dodecane	34.8	13.9	34.4	13.6	0.9228	0.1031	NS
TXIB	938	4.8	946	1.9	0.7906	0.2839	NS
TVOCs	4,140	15.6	3,960	19.3	0.7732	0.3083	NS

Table D-6 Dominant compounds emitted from second 15 minute air sample from wall covering 2 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	77.8	6.3	63.4	16.5	0.0977	2.1525	NS
n-Decane	325	4.4	298	18.3	0.4523	0.8313	NS
n-Undecane	206	7.9	200	15.8	0.7846	0.2923	NS
2-Ethylhexanoic acid	178	7.6	179	7.5	0.9318	0.0911	NS
n-Dodecane	28.5	8.8	28.0	12.0	0.8474	0.2052	NS
TXIB	1,050	5.7	1,050	4.1	1.0000	0.0000	NS
TVOCs	2,570	14.3	2,280	26.9	0.5202	0.7041	NS

Table D-7 Dominant compounds emitted from first 15 minute air sample from wall covering 2 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	184	76.9	193	42.7	0.9307	0.0925	NS
n-Decane	765	105	791	57.1	0.9634	0.0488	NS
n-Undecane	575	112	526	53.3	0.9098	0.1206	NS
2-Ethylhexanoic acid	1,010	62.5	714	37.0	0.4958	0.7484	NS
n-Dodecane	109	98.2	102	41.4	0.9210	0.1056	NS
TXIB	4,770	19.7	4,030	20.0	0.3587	1.0360	NS
TVOCs	8,340	126.4	8,160	65.0	0.9802	0.0264	NS

Table D-8 Dominant compounds emitted from second 15 minute air sample from wall covering 2 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	91.9	67.8	83.4	27.3	0.8352	0.2219	NS
n-Decane	455	102	431	55.9	0.9405	0.0795	NS
n-Undecane	379	115	324	59.0	0.8517	0.1994	NS
2-Ethylhexanoic acid	999	61.1	699	41.7	0.4852	0.7682	NS
n-Dodecane	77.1	108	68.0	54.6	0.8710	0.1730	NS
TXIB	4,800	19.4	4,090	20.0	0.3777	0.9911	NS
TVOCs	5,240	128	4,610	71.3	0.8901	0.1473	NS

Table D-9 Dominant compounds emitted from first 15 minute air sample from wall covering 3 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})			
	Tenax (n = 3)		MS2 (n = 2)	
	Mean	%RSD	Mean	%RSD
Toluene	9.6	3.8	11.1	Not applicable
2-Butoxyethanol	59.0	16.4	53.3	
Texanol	485	79.7	419	
TXIB	86.0	45.0	77.0	
TVOCs	957	65.6	699	

Table D-10 Dominant compounds emitted from second 15 minute air sample from wall covering 3 using μ-CTE at 23 ºC

Compound	Emission rate (μg m^{-2} h^{-1})			
	Tenax (n = 3)		MS2 (n = 1)	
	Mean	%RSD	Mean	%RSD
Toluene	Not detected	---	Not detected	Not applicable
2-Butoxyethanol	Not detected	---	Not detected	
Texanol	437	78.7	53.1	
TXIB	81.8	44.6	53.1	
TVOCs	601	85.4	28.0	

Table D-11 Dominant compounds emitted from first 15 minute air sample from wall covering 3 using µ-CTE at 40 ºC

Compound	Emission rate (µg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	3.3	5.4	5.9	19.0	0.0158	4.0279	S
2-Butoxyethanol	67.2	25.9	101	39.5	0.2490	1.3478	NS
Texanol	1,780	94.1	149	74.1	<0.0001	19.4436	S
TXIB	228	60.4	161	16.8	0.4548	0.8269	NS
TVOCs	2,490	93.9	281	60.8	1.6335	0.1777	NS

Table D-12 Dominant compounds emitted from second 15 minute air sample from wall covering 3 using µ-CTE at 40 ºC

Compound	Emission rate (µg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	Not detected	---	Not detected	---	---	---	---
2-Butoxyethanol	42.7	16.7	46.4	14.2	0.5447	0.6611	NS
Texanol	1,090	95.1	104	54.5	0.1741	1.6508	NS
TXIB	158	50	112	2.4	0.3689	1.0118	NS
TVOCs	1,520	99	132	73.0	0.1866	1.5920	NS

Table D-13 Dominant compounds emitted from third 15 minute air sample from wall covering 3 using µ-CTE at 40 ºC

Compound	Emission rate (µg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	Not detected	---	Not detected	---	---	---	---
2-Butoxyethanol	Not detected	---	Not detected	---	---	---	---
Texanol	306	79.5	62.0	27.8	0.1578	1.7348	NS
TXIB	81.6	21.5	52.7	4.5	0.0472	2.8338	S
TVOCs	550 [1]	---	19.9 [2]	---	---	---	--

[1] detectable in only 2 samples; [2] detectable in only 1 sample

Table D-14 Dominant compounds emitted from fourth 15 minute air sample from wall covering 3 using µ-CTE at 40 ºC

Compound	Emission rate (µg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	Not detected	---	Not detected	---	---	---	---
2-Butoxyethanol	Not detected	---	Not detected	---	---	---	---
Texanol	108 [1]	---	53.1 [2]	---	---	---	---
TXIB	27.7	9.4	25.5	6.0	0.2731	1.2695	NS
TVOCs	54.1 [1]	---	Not detected	---	---	---	---

[1] detectable in only 2 samples; [2] detectable in only 1 sample

Table D-15 Dominant compounds emitted from first 15 minute air sample from wall covering 4 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	27.7	7.3	32.5	5.8	0.0394	3.0138	S
n-Decane	52.2	6.9	58.9	6.6	0.0941	2.1865	NS
n-Undecane	36.8	5.5	43.1	10.0	0.0829	2.3009	NS
2-Ethylhexanoic acid	162	4.6	162	7.2	1.0000	0.0000	NS
n-Dodecane	11.0	7.1	12.3	14.5	0.3168	1.1431	NS
TXIB	18.1	24.0	17.5	3.1	0.8221	0.2401	NS
TVOCs	239	11.7	268	21.5	0.4773	0.7832	NS

Table D-16 Dominant compounds emitted from second 15 minute air sample from wall covering 4 using μ-CTE at 40 ºC

Compound	Emission rate (μg m^{-2} h^{-1})				Statistics		
	Tenax (n = 3)		MS2 (n = 3)		P	t	S/NS
	Mean	%RSD	Mean	%RSD			
Toluene	14.3	9.1	15.9	13.7	0.3391	1.0845	NS
n-Decane	34.3	5.5	37.8	5.0	0.0871	2.2561	NS
n-Undecane	25.7	8.6	28.5	6.0	0.156	1.7443	NS
2-Ethylhexanoic acid	174	4.8	173	4.0	0.8818	0.1584	NS
n-Dodecane	8.2	9.6	9.0	5.3	0.2158	1.4688	NS
TXIB	20.4	6.2	20.6	19.7	0.9397	0.0805	NS
TVOCs	124	23.0	126	15.4	0.9246	0.1007	NS

D.2 Supporting tables to check standard stability study

Table D-17 Amounts of target analytes found for the sets of tubes analysed immediately as part of the check standard stability study

Sorbent	Nominal mass (ng)	Humidity (%RH)	Amount found (ng on tube) Mean (%RSD) (n=5 for 100 ng loading levels and n=4 for 40 and 500 ng levels)								
			n-Hexane	MIBK	Toluene	Butyl acetate	Cyclohex-anone	Phenol	123-TMB	4-PCH	n-Hexa-decane
Tenax TA	100	<3	124 (1.9 %)	110 (1.4 %)	118 [b] (2.4 %)	112 (0.9 %)	111 (1.4 %)	112 (8.6 %)	88 (0.9 %)	88 (1.0 %)	28 (1.5 %)
Tenax TA	100	40 [a]	118 (3.5 %)	106 (2.1 %)	111 (2.2 %)	107 (2.1 %)	106 (1.9 %)	105 (5.5 %)	89 (2.7 %)	90 (3.2 %)	53 (5.4 %)
MS1	100	<3	126 (2.1 %)	106 (1.8 %)	115 (2.6 %)	107 (4.1 %)	104 (2.3 %)	112 (5.1 %)	85 (1.2 %)	85 (2.1 %)	28 (5.2 %)
MS1	100	40	124 (1.6 %)	104 (1.1 %)	111 (1.6 %)	104 (5.0 %)	103 (1.5 %)	110 (5.1 %)	87 (0.3 %)	88 (1.6 %)	49 (2.8 %)
MS2	100	40	126 (1.4 %)	105 (0.9 %)	112 (1.9 %)	105 (4.5 %)	104 (1.2 %)	120 (2.2 %)	84 (1.2 %)	85 (1.7 %)	26 (4.4 %)
MS1	40	40	52 (1.1 %)	42 (1.1 %)	52 (2.4 %)	43 (1.5 %)	43 (0.9 %)	55 (10 %) [c]	34 (1.0 %)	34 (0.6 %)	44 (2.5 %)
MS1	500	40	642 (2.4 %)	542 (1.7 %)	559 (2.5 %)	544 (1.9 %)	528 (2.0 %)	466 (3.8 %)	437 (0.4 %)	428 (0.7 %)	457 (1.1 %)

[a] Outlying results for all compounds on one tube removed; [b] One outlying toluene value removed; [c] One outlying phenol value removed

Table D-18 Comparison with results for QC tubes for the sets of tubes analysed immediately as part of the stability study

Sorbent	Nominal mass (ng)	Humidity (%RH)	% Recovery compared to amount found on QC tubes								
			n-Hexane	MIBK	Toluene	Butyl acetate	Cyclohex-anone	Phenol	123-TMB	4-PCH	n-Hexa-decane
Tenax TA	100	<3	115	104	116	122	100	109	101	111	98
Tenax TA	100	40	110	100	105	117	97	109	98	109	103
MS1	100	<3	117	100	107	116	94	109	98	107	98
MS1	100	40	116	98	104	113	94	115	97	107	96
MS2	100	40	115	99	103	118	96	112	97	102	99
MS1	40	40	117	101	95	129	104	129	104	117	100
MS1	500	40	119	100	104	112	92	89	94	101	100

Table D-19 Statistical comparison of the recoveries for the sets of tubes analysed immediately

Loading level and condition	Parameter	n-Hexane	MIBK	Toluene	Butyl acetate	Cyclo-hexanone	Phenol	123-TMB	4-PCH	n-Hexadecane
100 ng, Tenax TA	Humidity	S [a]	S	S	S	S	NS	NS	NS	NR [b]
100 ng, MS1	Humidity	NS	NS	S	NS	NS	NS	S	S	NR
100 ng, <3 %RH	Sorbent (only tested for Tenax TA and MS1)	NS	S	NS	S	S	NS	S	S	NS
100 ng, 40 %RH	Sorbent	S [c]	NS	NS	NS	NS	S [d]	S [d]	S [d]	S [e]

[a] S = significantly different and NS = not significantly different (P = 0.05 probability level)
[b] No tubes available for comparison; [c] No significant difference in recoveries between MS1 and MS2; [d] No significant difference in recoveries between Tenax TA and MS1; [e] Only Tenax TA and MS1 available to test

Table D-20 Statistical comparison of the recoveries from different sorbents and loading conditions after 4 weeks storage

Loading and storage conditions	Parameter	n-Hexane	MIBK	Toluene	Butyl acetate	Cyclo-hexanone	Phenol	123-TMB	4-PCH	n-Hexa-decane
100 ng, Tenax TA, RT	Humidity	NS	NS	S	NS	NS	S	NS	NS	NR
100 ng, MS1, RT	Humidity	NS	NS	NS	NS	NS	NS	NS	S	NR
100 ng, MS1, 5 °C	Humidity	NS	NS	NS	NS	NS	NS	NS	NS	NS
100 ng, <3 %RH, RT	Sorbent (only tested for Tenax TA and MS1)	S	NS	S	NS	NS	NS	NS	NS	S
100 ng, 40 %RH, RT	Sorbent	S [a]	NS	S [b]	NS	NS	NS	NS	NS	NS [c]

[a] No significant difference in recoveries between MS1 and MS2; [b] Significant difference only between Tenax TA and MS2; [c] Only Tenax TA and MS1 available to test

Appendix E Supporting information for Chapter 5

Table E-1 Concentrations of dominant compounds detected in the emissions from samples of PU foam trapped onto two sorbent types

Concentration (µg m^{-3})								
	n-Pentane		**MCB** †		**Butyl acetate**		**m/p-Xylene**	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	284	461	1,735	2,284	136	133	233	230
SD	114	148	431	534	95.7	90.9	148	139
Max	525	697	2,662	3,315	339	327	545	526
Min	162	284	1,289	1,765	64.4	63.5	120	119
n	9	9	9	9	7	7	7	7
P	0.0001		<0.001		0.1801		0.5065	
t	8.7682		11.655		1.5169		0.7063	
NS/S ¶	S		S		NS		NS	
	Styrene		**o-Xylene**		**2-Ethoxyethyl-acetate** †		**Benzaldehyde** †	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	3,470	3,410	150	147	281	253	162	166
SD	1,690	1,550	86.5	79.4	152	104	129	128
Max	6,890	6,500	334	316	586	419	431	425
Min	2,030	2,000	84.7	87.8	125	121	9.3	6.7
n	7	7	7	7	7	7	9	9
P	0.812		0.3101		0.2733		0.1125	
t	0.9449		1.1086		1.2057		1.7823	
NS/S	NS		NS		NS		NS	

† quantified using toluene response factor

¶ NS = not significantly different at the P = 0.05 probability level, S = significantly different at the P = 0.05 probability level

Table E-2 Concentrations of compounds detected in smaller amounts in the emissions from samples of PU foam trapped onto two sorbent types

Concentration (µg m^{-3})								
	MIBK		**Toluene**		**Ethylbenzene**		**1-methoxy-2-propylacetate** †	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	30.3	30.2	33.6	37.2	41.3	41.1	66.6	64.6
SD	16.0	15.2	30.7	33.8	26.1	25.1	36.9	35.8
Max	62.2	60.9	98.3	97.2	95.4	93.8	145.5	140.6
Min	16.4	16.2	5.6	7.3	19.6	19.8	37.3	34.7
n	7	7	9	9	7	7	9	9
P	0.8436		0.2913		0.6526		0.0324	
t	0.2060		1.1298		0.4736		2.7697	
NS/S	NS		NS		NS		S	
	Benzene-acetaldehyde †		**Epoxyethyl-benzene** †		**Unidentified ester** †		**Benzoic acid** †	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	36.0	63.2	65.6	21.8	36.0	63.2	65.6	21.8
SD	16.6	40.7	44.3	10.1	16.6	40.7	44.3	10.1
Max	56.5	144	145	33.4	20.8	22.2	39.6	40.2
Min	10.1	20.6	18.5	7.6	111.1	11.8	11.2	9.2
n	7	7	6	6	7	7	6	6
P	0.0778		0.0747		0.1751		0.5574	
t	2.1248		2.2457		1.6462		0.6160	
NS/S	NS		NS		NS		NS	

† quantified using toluene response factor

Table E-3 Concentrations of dominant compounds detected in the emissions from samples of foam sealant trapped onto two sorbent types with sample volume 0.5-1.5 litres

Concentration (µg m^{-3})								
	Dimethyl ether †		**Isobutane †**		**n-Butane †**		**Isopentane †**	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	758	571	2,120	3,700	771	2,390	38.6	247
SD	607	491	1,980	1,720	1,030	2,160	50.6	340
Max	2,140	1,630	7,230	7,580	3,450	7,500	136	826
Min	29.4	132	255	1,820	4.5	187	3.4	14.2
n	9	9	11	11	11	11	8	8
P	0.2179		0.0024		0.0011		0.0821	
t	1.3373		4.0276		4.5429		2.0287	
NS/S	NS		S		S		NS	

	RT ‡ 10.6 min Siloxane †		**RT 23.9 min Siloxane †**		**OMCTS †, §**		**RT 32.8 min Siloxane †**		**DMCPS †, ¶**	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	251	246	296	290	496	495	208	200	317	295
SD	399	380	450	447	1,190	1,200	301	297	503	477
Max	1,060	1,030	1,120	1,150	3,850	3,870	745	768	1,300	1,300
Min	14.2	12.9	8.3	8.3	18.8	15.2	12.9	11.3	5.4	5.5
n	9	9	8	8	10	10	7	7	8	8
P	0.9053		0.5388		0.9981		0.5305		0.9298	
t	0.1228		0.6461		0.0024		0.6655		0.0897	
NS/S	NS		NS		NS		NS		NS	

† Unidentified or only tentatively identified from NIST library, no pure standard available to confirm identity, quantified using response factor for toluene; ‡ RT = retention time;
§ OMCTS = Octamethylcyclotetrasiloxane; ¶ DMCPS = Decamethylcyclopentasiloxane

Table E-4 Concentrations of compounds detected in smaller amounts in the emissions from samples of foam sealant trapped onto two sorbent types with sample volume 0.5-1.5 litres

Concentration (µg m^{-3})								
	Propan-2-ol		**n-Hexane**		**Methyl-cyclopentane** †		**1,4-Dioxane**	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	66.4	120	159	208	52.1	96.2	79.9	84.0
SD	73.5	160	234	318	62.1	119	72.2	74.6
Max	255	587	576	845	139	283	221	240
Min	13.4	16.1	6.4	6.4	6.0	9.8	22.3	25.7
n	11	11	9	9	6	6	7	7
P	0.0908		0.1473		0.1391		0.3493	
t	1.8714		1.6045		1.7581		1.015	
NS/S	NS		NS		NS		NS	

	n-Hexanal		**RT 38.1 min Siloxane** †		**RT 39.9 min Siloxane** †		**RT 41.3 min Siloxane** †		**n-Tetra-decane**	
	Tenax	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	87.9	82.1	89.7	84.9	36.0	33.6	26.2	25.0	29.4	28.5
SD	78.4	72.5	108	105	39.0	37.1	14.1	15.9	15.8	15.4
Max	234	230	297	298	108	109	50.1	55.7	57.6	56.4
Min	4.1	3.9	11.7	10.3	5.7	5.6	10.8	11.7	4.7	5.2
n	8	8	7	7	7	7	7	7	7	7
P	0.3702		0.4247		0.3807		0.5542		0.3919	
t	0.9576		0.8564		0.946		0.6263		0.9225	
NS/S	NS		NS		NS		NS		NS	

† Unidentified or only tentatively identified from NIST library, no pure standard available to confirm identity, quantified using response factor for toluene

Table E-5 Concentrations of compounds showing some effect of sorbent, sample volume 1.5-5.0 litres

Concentration (μg m^{-3})								
Compound	**Isopentane**		**Propan-2-ol**		**n-Hexane**		**Methyl-cyclopentane**	
Sorbent	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**	**Tenax**	**MS1**
Mean	9.5	60.9	32.5	70.2	33.1	39.9	10.4	18.4
SD	6.5	58.6	19.1	31.2	36.8	44.9	7.2	13.9
Max	19.9	172	65.3	131	109	135	21.2	41.0
Min	3.3	14.2	11.9	24.6	1.1	1.4	3.0	5.9
n	6	6	8	8	8	8	5	5
P	0.0615		0.0012		0.0581		0.0612	
t	2.4016		5.2700		2.2622		2.5814	
S/NS	NS		S		NS		NS	

Appendix F Lists of chemicals of interest

F.1 Chemicals occurring on one or more lists of target compounds

Table F-1 Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on ¶	Compound	CAS No.	List(s) on
Acetaldehyde	75-07-0	a,b,d,e,f,i,j,k, m,n,o	4-Amino-3-fluorophenol	399-95-1	c
Acetamide	60-35-5	j,k	p-Amino-azobenzene	60-09-3	c,k
Acetic acid	64-19-7	a,d,e,n	o-Aminoazo toluene	97-56-3	c,k
Acetohydroxamic acid	546-88-3	k	4-Amino-biphenyl	92-67-1	c,j,k
Acetone	67-64-1	a,d	2-Aminoethanol	141-43-5	n
Acetonitrile	75-05-8	j	2-Amino-fluorene	153-78-6	k
Acetophenone	98-86-2	a,d,e,j,n,o	Bis(4-amino-phenyl)methane	101-77-9	b,c,g,h,n
2-Acetylamino-fluorene	53-96-3	j,k	2-Amino-pyridine	504-29-0	n
Acetylene tetrabromide	79-27-6	n	n-Amyl acetate	628-63-7	n
Acrolein	107-02-8	j,n	tert-Amyl acetate	625-16-1	n
Acrylamide	79-06-1	b,c,h,j,k,n	tert-Amyl methyl ether	994-05-8	k,n
Acrylic acid	79-10-7	j,n,o	Aniline	62-53-3	a,j,k,n,o
Adipic acid	1240-04-9	n	p-Anisidine	29191-52-4	n
Adiponitrile	111-69-3	n	Azobenzene	103-33-3	c,g,k
Allyl alcohol	107-18-6	n	Benzaldehyde	100-52-7	a,d,e
Allyl chloride	107-05-1	j,n	Benzene	71-43-2	a,b,c,f,g,h,i,j, k,l,m,n,o
Allyl glycidyl ether	106-92-3	n	Benzene, 1,2-dimethoxy-4-(2-propenyl)	93-15-2	k,o
Allyl propyl disulfide	2179-59-1	n	Benzofuran	271-89-6	k
Alpha,alpha-chlorotoluene	98-87-3	c	Benzoic trichloride	98-07-7	c,g,h,j,k,n

¶ see Table 2-1 for key to lists of chemicals

Table F-1 (contd.1) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Benzothiazole	95-16-9	m,o	1-Butyl acetate	123-86-4	a,d,e,l,n,o
Benzoyl chloride	98-88-4	n	sec-Butyl acetate	105-46-4	n
Benzyl acetate	140-11-4	n	tert-Butyl	540-88-5	n
Benzyl alcohol	100-51-6	d,e	n-Butyl acrylate	141-32-2	d,e,n,o
Benzyl chloride	100-44-7	c,g,h,j,k,n	n-Butyl formate	592-84-7	a,d,e
Biphenyl	92-52-4	j,n	n-Butyl glycidyl ether	2426-08-6	k,n
Bis (chloro-methyl) ether	542-88-1	c,h,j,k,n	Butyl glycolate	7397-62-8	d,e
Bis(2-chloro-1-methylethyl)ether	108-60-1	k	n-Butyl lactate	138-22-7	n
Bis(2-Dimethyl-aminoethyl) ether	3033-62-3	n	n-Butylamine	109-73-9	n
Bis(2-ethyl-hexyl)phthalate	117-81-7	a,f,j,k	Butylated hydroxyanisole	25013-16-5	k
Bromochloro-acetic acid	5589-96-8	k	Butylated hydroxytoluene	128-37-0	a,d,e,n,o
Bromochloro-methane	74-97-5	n	n-Butylbenzene	104-51-8	a,d,e
Bromodichloro-methane	75-27-4	k	Butyric acid	107-92-6	a,d,e
Bromoethane	74-96-4	k,n	Butyrolactone	96-48-0	d,e,k
Bromoform	75-25-2	j,k	C11- C13 alcohols	112-53-8	d,o
1-Bromopropane	106-94-5	k,n,o	C4- C10 alcohols	78-92-2	d,n,o
2-Bromopropane	75-26-3	k,o	Camphene	79-92-5	a
Butanal	123-72-8	a,d,e	Camphor	76-22-2	n
1,4-Butandiol	110-63-4	d,e	n-Caproic acid	142-62-1	a,d,e,o
Butanethiol	109-79-5	n	Caprolactam	105-60-2	a,d,e,j,m,n,o
1-Butanol	71-36-3	a,d,e,l,n,o	Carbon disulfide	75-15-0	i,j,k,n,o
tert-Butanol	75-65-0	a,d,e,n	Carbon tetrachloride	56-23-5	a,e,i,j,k,n
2-Butanonoxime	96-29-7	d,e	3-Carene	13466-78-9	a,e,n
2,4-Butansultone	1121-03-5	c	3-Carene, 1S	498-15-7	d
2-Butenal	4170-30-3,	a,d,e,n	b-Caryophyllene	87-44-5	a
2-Butoxyethyl acetate	112-07-2	a,d,e,n	Catechol	120-80-9	j,k,n

Table F-1 (contd.2) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
α-Cedrene	469-61-4	a	Chloromethyl methyl ether	107-30-2	c,j,k
Chlorinated diphenyl oxide	31242-93-0	n	4-Chloro-*o*-phenylene-diamine	95-83-0	k
Chlorine-2,3-epoxypropane	106-89-8	b,c,h,i,j,k,n,o	5-Chloro-*o*-toluidine	95-79-4	k
R-1-chlorine-2, 3-epoxypropane	51594-55-9	c,g	p-Chloro-*o*-toluidine, hydrochloride	3165-93-3	k
1-Chloro-1-nitropropane	600-25-9	n	Chloroprene	126-99-8	h,j,k,n,o
2-Chloro-1-propanol	78-89-7	n	2-Chloro-propionic acid	598-78-7	k,n
5-Chloro-2-methyl-2H-isothiazol-3-one (CIT)	26172-55-4	d,e	o-Chlorostyrene	2039-87-4	n
4-Chloro-2-methyl-benzene amine	95-69-2	c,g,h,k	o-Chloro-toluene	95-49-8	n
3-Chloro-2-methylpropene	563-47-3	k	Chrysene	218-01-9	c,h
1-Chloro-2-propanol	127-00-4	n	o-Cresol	95-48-7	j
1-Chloro-4-nitrobenzene	100-00-5	k,n	m-Cresol	108-39-4	j,o
Chloro-acetaldehyde	107-20-0	n	p-Cresol	106-44-5	j,o
Chloroacetic acid	79-11-8	j,n	Cresols (isomers and mixtures)	1319-77-3	j,n
Chloroacetone	78-95-5	n	Crufomate	299-86-5	n
2-Chloro-acetophenone	532-27-4	j,n	Cumene	98-82-8	a,d,e,j,k,n,o
Chloroacetyl chloride	79-04-9	n	Cyclohexane	110-82-7	a,d,e,l,n,o
4-Chloroaniline	106-47-8	c,g,h,k	Cyclohexanol	108-93-0	a,d,e,n
p-Chloroaniline hydrochloride	20265-96-7	k	Cyclohexanone	108-94-1	a,d,e,n,o
Chlorobenzene	108-90-7	a,i,j,n,o	Cyclohexene	110-83-8	n
o-Chloro-benzylidene malononitrile	2698-41-1	n	Cyclo-hexylamine	108-91-8	n
Chloroform	67-66-3	i,j,k,n,o	Cyclopentadiene	542-92-7	n

Table F-1 (contd.3) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Cyclopentane	287-92-3	N	2-N-Dibutyl-aminoethanol	102-81-8	n
Cyclopentanone	120-92-3	a,d,e	1,1-Dichloro-1-nitroethane	594-72-9	n
Decahydro-naphthalene	91-17-8	e	1,4-Dichloro-2-butene	764-41-0	c,h,k,n
Decamethyl-cyclopenta-siloxane (D5)	541-02-6	d,e	1,3-Dichloro-2-propanol	96-23-1	c,g,h,o
Decanal	112-31-2	a,d,e,o	Dichloroacetic acid	79-43-6	k,n
2-Decenal	3913-71-1, 2497-25-8, 3913-81-3	a,d,e	Dichloro-acetylene	7572-29-4	n
1-Decene	872-05-9	a	p-Dichloro-benzene	106-46-7	a,e,f,i,j,k,n,o
N,N'-Diacetyl-benzidine	613-35-4	k	o-Dichloro-benzene	95-50-1	n
2,4-Diamino-anisole	615-05-4	c,h,k	3,3'-Dichloro-benzidine	91-94-1	c,h,j,k
4,4'-Diamino-diphenyl ether	101-80-4	c,k	1,2-Dichloro-ethane	107-06-2	a,c,g,h,j,k,n,o
1,2-Diamino-ethane	107-15-3	n	1,1-Dichloro-ethane	75-34-3	j,k
Diamino-toluene (mixed)	25376-45-8	h,k	Dichloroethyl ether	111-44-4	j,k,n,o
Diazoamino-benzene	136-35-6	k	1,1-Dichloro-ethylene	75-35-4	i,j,n
1,2-Dibromo-3-chloropropane	96-12-8	c,h,j,k	Dichloro-methane	75-09-2	a,b,i,j,k,n,o
Dibromoacetic acid	631-64-1	k	1,2-dichloro-propane	78-87-5	j,k,n,o
1,2-Dibromo-ethane	106-93-4	c,g,h,j,k,n	1,3-dichloro-propene (1)	10061-01-5 or 542-75-6	c,g,j,k,n
2,3-Dibromo-propan-1-ol	96-13-9	c,g,h,k	2,2-Dichloro-propionic acid	75-99-0	n
Dibutyl fumarate	105-75-9	d	1,3-Dicyclo-pentadiene	77-73-6	n
Dibutyl glutarate	71195-64-7	d	Diepoxybutane	1464-53-5	c,k
Dibutyl phthalate	84-74-2	a,f,j,k	Diethanolamine	111-42-2	j,n
Dibutyl succinate	925-06-4	d	1,2-Diethoxy-ethane	73506-93-1	d,e

Table F-1 (contd.4) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Diethyl ether	60-29-7	n	1,3-Diisopropyl-benzene	99-62-7	a,d,e
Diethyl ketone	96-22-0	n	1,4-Diisopropyl-benzene	100-18-5	a,d,e
Diethyl phthalate (DEP)	84-66-2	n	3,3-dimethoxy-benzidine	119-90-4	c,g,h,j,k
Diethyl sulfate	64-67-5	c,g,h,j,k	1,2-Dimethoxy-ethane	110-71-4	a,d,e
Diethylamine	109-89-7	n	Dimethoxy-methane	109-87-5	a,n
2-Diethyl-aminoethanol	100-37-8	n	Dimethyl adipate	627-93-0	d,e
Diethylene glycol	111-46-6	d,e	Dimethyl aminoazo-benzene	60-11-7	j,k
Diethylene glycol monomethyl ether acetate	124-17-4	d,e	Dimethyl carbamyl chloride	79-44-7	c,g,h,j,k
Diethylene glycol phenyl ether	104-68-7	d	Dimethyl disulfide	624-92-0	n
Diethylene glycol-monobutylether	112-34-5	a,d,e,o	Dimethyl glutarate	1119-40-0	d,e
Diethylene triamine	111-40-0	n	1,1-Dimethyl hydrazine	57-14-7	c,j,k,n
1,2-Diethyl-hydrazine	1615-80-1	k	Dimethyl phthalate	131-11-3	a,j,n
Difluoro-dibromomethane	75-61-6	n	Dimethyl succinate	106-65-0	d,e
Diglycidyl ether	2238-07-5	k,n	Dimethyl sulfate	77-78-1	c,g,h,j,k
Diglycidyl resorcinol ether	101-90-6	k	2,6-Dimethyl-4-heptanone	108-83-8	n
Dihydrosafrole	94-58-6	k	N,N-Dimethyl-acetamide	127-19-5	k,n
Dihydroxy-benzene	123-31-9	n	2,6-Dimethyl-aniline	87-62-7	k,n
Diisopropyl sulfate	2973-10-6	k	Dimethylaniline	121-69-7	n
Diisopropyl-amine	108-18-9	n	2,2-Dimethyl-butane	75-83-2	n

Table F-1 (contd.5) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
2,3-Dimethyl-butane	79-29-8	n	1,3-Dioxalane	646-06-0	n
1,4-Dimethyl-cyclohexane (cis + trans)	589-90-2	a	1,4-Dioxan	123-91-1	a,b,d,e,i,j,k, n,o
Dimethylethoxy-silane	14857-34-2	n	Diphenylamine	122-39-4	n
Dimethylform-amide (DMF)	68-12-2	d,i,j,n,o	1,2-Diphenyl-hydrazine	122-66-7	c,g,h,j,k
1,2-Dimethyl-hydrazine	540-73-8	c,h,k	Dipropyl ketone	123-19-3	n
3,5-Dimethyl-octane	15869-93-9	a	Dipropylene glycol	106-62-7, 110-98-5, 25265-71-8	d,e
Dimethyl-sulfamoyl chloride	13360-57-1	c	Dipropylene glycol dimethyl ethers	63019-84-1, 89399-28-0, 111109-77-4	d,e
Dimethylvinyl-chloride	513-37-1	k	Dipropylene glycol mono-methyl ether	34590-94-8	d,e,n,o
Dinitolmide	148-01-6	n	Dipropylene glycol mono-methyl ether acetate	88917-22-0	d,e
m-Dinitrobenzene	99-65-0	k,n	Dipropylene glycol-mono-n-butylether	29911-28-2, 35884-42-5	d,e
o-Dinitrobenzene	528-29-0	k,n	Dipropylene glycol-mono-n-propylether	29911-27-1	d,e
p-Dinitrobenzene	100-25-4	k,n	Dipropylene glycol-mono-t-butylether	132739-31-2	d
3,5-Dinitroluene	618-85-9	c	Divinyl benzene	1321-74-0	n
2,5-Dinitroluene	619-15-8	c	Dodecamethyl-cyclohexa-siloxane (D6)	540-97-6	d
4,6-Dinitro-o-cresol	534-52-1	n	n-Dodecane	112-40-3	a,l,o
2,4-Dinitrophenol	51-28-5	j	Dodecyl mercaptan	112-55-0	n
2,3-Dinitrotoluene	602-01-7	c,g,h	Enflurane	13838-16-9	n
Dinitrotoluene	25321-14-6	c,n	R-2,3-Epoxi-1-propanol	57044-25-4	c

Table F-1 (contd.6) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
1,2-Epoxybutane	106-88-7	j,n,o	Ethylene imine	151-56-4	c,h,j,k,n
Estragole	140-67-0	k,o	Ethylene thiourea	96-45-7	j,k
Ethandiol	107-21-1	d,e,i,j,n,o	2-Ethylhexanal	123-05-7	a,d,e
Ethanethiol	75-08-1	n	2-Ethylhexane acid	149-57-5	d,e,k,m,n,o
Ethanol	64-17-5	d	2-Ethylhexyl acetate	103-09-3	a,d,e,o
2-Ethoxyethanol	110-80-5	a,b,d,e,i,k,n,o	2-Ethylhexyl acrylate	103-11-7	d,e,o
2-Ethoxyethyl acetate	111-15-9	a,b,d,e,i,k,n,o	Ethylidene norbornene	16219-75-3	n
Ethyl acetate	141-78-6	a,d,n,o	Ethylmethyl-ketone	78-93-3	a,d,e,j,n.o
Ethyl acrylate	140-88-5	a,d,e,j,k,n	n-Ethyl-morpholine	100-74-3	n
Ethyl amyl ketone	541-85-5	n	Ethyl-tert-butyl ether	637-92-3	k,n
Ethylbenzene	100-41-4	a,d,e,f,i,j,k,l, n,o	2-Ethyltoluene	611-14-3	a,d,e
Ethyl butyl ketone	106-35-4	n	3-Ethyl-toluene/ 4-Ethyltoluene	620-14-4/ 622-96-8	a
Ethyl carbamate	51-79-6	c,j,k	Formaldehyde	50-00-0	b,e,f,i,j,k,m, n,o
Ethyl cyanoacrylate	7085-85-0	n	Formamide	75-12-7	n
Ethyl dipropyl-thiocarbamate	759-94-4	k	Formic acid	64-18-6	n
Ethyl formate	109-94-4	n	Furan	110-00-9	c,g,k
Ethyl methanesulfonate	62-50-0	k	Furfural	98-01-1	a,d,e,n,o
2-Ethyl-1-hexanol	104-76-7	a,d,e,m,o	Furfuryl alcohol	98-00-0	n
Ethyldiglycol	111-90-0	d,e	Glutardialdehyde	111-30-8	d,e,n
Ethylene carbonate	96-49-1	d,e	Glycidaldehyde	765-34-4	k
Ethylene chlorohydrin	107-07-3	n	Glycidol	556-52-5	c,k,n
Ethylene glycol dinitrate	628-96-6	n	Gyromitrin	16568-02-8	k
Ethylene glycol-monobutylether	111-76-2	a,d,e,f,j,l,n,o	Halothane	151-67-7	k

Table F-1 (contd.7) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Heptanal	111-71-7	a,d,e,o	n-Hexane	110-54-3	a,d,e,i,j,l,n,o
n-Heptane	142-82-5	a,d,n,o	Hexane, other isomers		n
n-Heptanoic acid	111-14-8	a,d,e	1,6-Hexane-diamine	124-09-4	n
2-Heptenal	AgBB: 2463-63-0, 18829-55-5, 29381-66-6 ISO: 57266-861	a,d,e	1-Hexanol	111-27-3	a,d,e
			Hexasiloxane, tetradecamethyl	107-52-8	o
Hexachloro-benzene	118-74-1	c,j,k,n	2-Hexenal	16635-54-4, 6728-26-3, 505-57-7, 1335-39-3	d,e
Hexachloro-butadiene	87-68-3	j,n	1-Hexene	592-41-6	n
Hexachloro-cyclopentadiene	77-47-4	j,n	2-Hexoxy-ethanol	112-25-4	d,e
Hexachloroethane	67-72-1	j,k,n,o	2-(2-Hexoxy-ethoxy)-ethanol	112-59-4	d,e
n-Hexadecane	544-76-3	a	sec-Hexyl acetate	108-84-9	n
Hexadecanoic acid	57-10-3	a	Hexylene glycol	107-41-5	d,n
2,4-Hexadienal (89 % trans, trans isomer; 11 % cis, trans isomer)	142-83-6	k	Hydroquinone	123-31-1	j
Hexamethylene diacrylate	13048-33-4	d,e	4-Hydroxy-4-methyl-pentane-2-one	123-42-2	d,e,n,o
Hexamethylene-1,6-diisocyanate	822-06-0	j	1-Hydroxy-acetone	116-09-6	d,e
Hexamethylene-tetramine	100-97-0	d,e	2-Hydroxy-propyl acrylate	999-61-1	n
Hexamethyl-phosphoramide	680-31-9	c,j,k	Indene	95-13-6	d,e,n
Hexanal	66-25-1	a,d,e,l	Isoamyl alcohol	123-51-3	n

Table F-1 (contd.8) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Isobutyl acetate	110-19-0	a,d,e,n,o	Linalool acetate	115-95-7	a,e
Isobutyl nitrite	542-56-3	h,k,n	Longifolene	475-20-7	a,o
Isobutyric acid	79-31-2	a,d,e	Maleic acid dibutylester	105-76-0	d
Isododecane	31807-55-3	a	Maleic anhydride	108-31-6	j,n
Isooctyl alcohol	26952-21-6	n	Mechlor-ethamine	51-75-2	c,k
Isooctylacrylate	29590-42-9	m	Mesityl oxide	141-79-7	n
Isopentane	78-78-4	n	Methacrylic acid	79-41-4	n
Isopentyl acetate	123-92-2	n	1-Methoxy propanol-2	107-98-2	a,d,e,i,n,o
Isophorone diisocyanate	4098-71-9	n	3-Methoxy-1-butanol	2517-43-3	d
Isoprene	78-79-5	k	2-Methoxy-1-methylethyl acetate	108-65-6	d,e,o
Isopropyl acetate	108-21-4	a,d,e,n	2-Methoxy-1-propanol	1589-47-5	d,e
Isopropyl ether	108-20-3	n	2-Methoxy-1-propyl acetate	70657-70-4	d,e
Isopropyl glycidyl ether	4016-14-2	n	1-Methoxy-2-(2-methoxy-ethoxy)-ethane	111-96-6	d,e
1-Isopropyl-2-methylbenzene	527-84-4	d,e	2-methoxy-5-methylbenzene amine	120-71-8	c,g,h,k
1-Isopropyl-3-methylbenzene	535-77-3	d	2-methoxy-aniline	90-04-0	c,g,h,j,k,n
1-Isopropyl-4-methylbenzene	99-87-6	d,o	2-Methoxy-ethanol	109-86-4	a,b,d,e,i,k,n,o
Isopropylamine	75-31-0	n	2-Methoxyethyl acetate	110-49-6	a,b,d,e,i,k,n,o
n-Isopropyl-aniline	768-52-5	n	4-Methoxy-phenol	150-76-5	n
Limonene	138-86-3	a,d,e,o	Methyl 2-cyanoacrylate	137-05-3	n

Table F-1 (contd.9) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Methyl acetate	79-20-9	d	Methyl silicate	681-84-5	n
Methyl acrylamide-methoxyacetate	77402-03-0	c,h	Methyl t-butyl ether	1634-04-4	i,j,n
Methyl acrylate	96-33-3	a,d,e,n	Methyl vinyl ketone	78-94-4	N
Methyl amyl alcohol	108-11-2	n	4-Methyl-1,2-dinitrobenzene	610-39-9	c,g,h
N-Methyl aniline	100-61-8	n	2-Methyl-1,3-dinitrobenzene	606-20-2	c,g,h,k
Methyl biphenyl	643-93-6	m	2-Methyl-1-propanol	78-83-1	a,d,e,n,o
Methyl carbamate	598-55-0	k	1-Methyl-2,4-dinitrobenzene	121-14-2	c,g,h,j,k
Methyl cyclohexane	108-87-2	a,d,e,n	1-Methyl-2-nitrobenzene	88-72-2	c,g,h,k,n
Methyl ethyl ketone peroxide	1338-23-4	n	1-Methyl-2-propylbenzene	1074-17-5	a,e
Methyl formate	107-31-3	e,n	N-Methyl-2-pyrrolidon	872-50-4	a,d,e,k,m,o
Methyl hydrazine	60-34-4	j,k,n	1-Methyl-3-nitro-1-nitroso-guanidine	70-25-7	c,h,k
Methyl iodide	74-88-4	j,k	1-Methyl-3-propylbenzene	1074-43-7	a,e
Methyl isoamyl ketone	110-12-3	n	2-Methyl-4-isothiazoline-3-on (MIT)	2682-20-4	d,e
Methyl methacrylate	80-62-6	a,d,e,j,n,o	1-Methyl-4-methylethyl-cyclohexane (cis/trans)	6069-98-3/ 1678-82-6	1
Methyl methanesulfonate	66-27-3	k	2-Methyl-5-nitrobenzene amine	99-55-8	c,g
Methyl n-amyl ketone	110-43-0	n,o	Methyl-acrylonitrile	126-98-7	n
Methyl n-butyl ketone	591-78-6	k,n,o	Methylazoxy-methanol acetate	592-62-1	c,k
Methyl propyl ketone	107-87-9	n	3-Methyl-butanone-2	563-80-4	a,d,e,n

Table F-1 (contd.10) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
1-Methylbutyl-acetate	626-38-0	n	Mustard Gas	505-60-2	c,k
2-Methylbutyl-acetate	624-41-9	n	N,N-Diethyl aniline	91-66-7	j
Methylcyclo-hexanol	25639-42-3	n	Naphthalene	91-20-3	a,d,e,i,j,k,m, n,o
2-Methylcyclo-hexanone	583-60-8	a,d,e,n	1-Naphthylamine	134-32-7	k
Methylcyclo-pentane	96-37-7	a	2-Naphthylamine	91-59-8	c,h,k
2-Methylcyclo-pentanone	1120-72-5	a,d,e	α-Naphthyl-thiourea	86-88-4	n
4-Methyldecane	2847-72-5	a	Neopentyl glycol	126-30-7	d
4,4-Methylene-bis (2-chloro-aniline)	101-14-4	c,j,k	Nicotine	54-11-5	k,n
4,4'-Methylene bis(2-methyl-aniline)	838-88-0	c,h,k	Nitrapyrin	1929-82-4	n
2-Methylethoxy-ethanol	109-59-1	d,e,n	5-Nitro-acenaphthene	602-87-9	c,k
2-Methylhexane	591-76-4	a	p-Nitroaniline	100-01-6	n
3-Methylhexane	589-34-4	a	2-Nitroanisol	91-23-6	c,g,h,k
Methyl isobutyl-ketone (MIBK)	108-10-1	a,d,e,j,l,n,o	Nitrobenzene	98-95-3	a,j,k,n
Methylisocyanate	624-83-9	n	4-Nitrobiphenyl	92-93-3	c,h,j,k
4-Methyl-m-phenylene-diamine	95-80-7	b,c,g,h,j,k	Nitroethane	79-24-3	n
2-Methylnonane	871-83-0	a	Nitromethane	75-52-5	k,n
2-Methyloctane	3221-61-2	a	2-Nitro-naphthalene	581-89-5	c,h
3-Methyloctane	2216-33-3	a	4-Nitrophenol	100-02-7	j
N-Methylol-acrylamide	924-42-5	k	2-Nitropropane	79-46-9	c,g,h,j,k,n,o
2-Methylpentane	107-83-5	a,n	1-Nitropropane	108-03-2	n
3-Methylpentane	96-14-0	a,d,n	N-Nitroso-diethylamine	55-18-5	c,k
Morpholine	110-91-8	n	N-Nitroso-dimethylamine	62-75-9	c,j,k

Table F-1 (contd.11) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
N-Nitroso-di-*n*-butylamine	924-16-3	c,k	Nonanal	124-19-6	a,d,e,m,o
N-Nitrosodi-isopropylamine	601-77-4	c	n-Nonane	111-84-2	a,n,o
N-Nitrosodi-*n*-propylamine	621-64-7	c,k	2-Nonenal	2463-53-8, 30551-15-6, 18829-56-6, 60784-31-8	a,d,e
N-Nitroso-diphenylamine	86-30-6	k	Octamethylcyclo-tetrasiloxane (OMCTS)	556-67-2	d,e
N-Nitrosoethyl-phenylamine	612-64-6	c	Octanal	124-13-0	a,d,e,m,o
N-Nitrosomethyl-ethylamine	10595-95-6	c,k	n-Octanoic acid	124-07-2	a,d,e
N-Nitroso-methyl-vinylamine	4549-40-0	k	1-Octanol	111-87-5	a,d,e
N-Nitroso-morpholine	59-89-2	c,j,k	2-Octenal	2363-89-5, 25447-69-2, 20664-46-4, 2548-87-0	d,e,o
N-Nitroso-n-ethylurea	759-73-9	k	1-Octene	111-66-0	a
N-Nitroso-n-methylurea	684-93-5	j,k	Other acrylates (acrylic acid ester)		d,e
N-Nitroso-n-methylurethane	615-53-2	k	Other alkylbenzenes, as long as individual isomers have not to be evaluated differently		d
N-Nitroso-nornicotine	16543-55-8	k	Other methacrylates		d,e
N-Nitroso-piperidine	100-75-4	c,k	Other saturated aliphatic hydrocarbons, up to C_8		a,d,e,n
1-Nitroso-pyrrolidin	930-55-2	c,g,k	Other saturated hydrocarbons, C_9-C_{16}	124-18-5	a,d,e,l
3-Nitrotoluene	99-08-1	n	Other terpene hydrocarbons		d,e
4-Nitrotoluene	99-99-0	n	p,p'-Oxybis(benzene-sulfonyl hydrazide)	80-51-3	k

Table F-1 (contd.12) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Pentachloro-nitrobenzene	82-68-8	n	1-Phenyl undecane and isomers	6742-54-7, 4537-15-9	a,d,e
Pentachloro-phenol	87-86-5	j,k,n	3-Phenyl-1-propanol	6180-61-6	a
n-Pentadecane	629-62-9	a,o	1-Phenyldecane and isomers	104-72-3, 4537-11-5	a,d,e
2,4,6,6-Pentamethyl-heptane	13475-82-6	a	o-Phenylene-diamine	95-54-5	k,n
Pentanal	110-62-3	a,d,e,n	p-Phenylene-diamine	106-50-3	j,n
Pentanol (all isomers)	71-41-0, 30899-19-5, 94624-12-1, 6032-29-7, 548-02-1, 137-32-6, 123-51-3, 598-75-4, 75-85-4, 75-84-3	a,d,e,o	m-Phenylene-diamine	108-45-2	n
			Phenylhydrazine	100-63-0	c,k
			o-Phenylphenol	90-43-7	k,o
2-Pentenal	1576-87-0, 764-39-6, 31424-04-1	a,d,e	Phenyl-phosphine	638-21-1	k
3-Pentyl acetate	620-11-1	n	2-Phenyl-propene	98-83-9	a,d,e,n
2-Pentylfuran	3777-69-3	a	Phthalic anhydride	85-44-9	j,n
Perchloromethyl-mercaptan	594-42-3	n	m-Phthalo-dinitrile	626-17-5	n
Phenol	108-95-2	a,d,e,i,j,m, n,o	Picric acid	88-89-1	n
Phenothiazine	92-84-2	n	α-Pinene	80-56-8	a,d,e,l,n,o
2-Phenoxy-ethanol	122-99-6	a,d,e	β-Pinene	127-91-3	a,d,e,o
Phenyl acetylene	536-74-3	a,d,e	Pivalic acid	75-98-9	a,d,e
4-Phenylcyclo-hexene (4-PCH)	4994-16-5	a,d,e,m,o	Propanal	123-38-6	a,d,e,j,n
Phenyl glycidyl ether	122-60-1	c,k	1,3-Propane sultone	1120-71-4	c,h,j,k
Phenyl octane and isomers	2189-60-8, 777-22-0	a,d,e	1-Propanol	71-23-8	a,d,n

Table F-1 (contd.13) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
2-Propanol	67-63-0	a,d,i,n,o	Propylene glycol mono-*t*-butyl ether	57018-52-7	k
2-Propanol, 1-(2-methoxy-propoxy)-	13429-07-7	o	1,2-Propylene glycol n-butyl ether	5131-66-8, 29387-86-8, 15821-83-7, 63716-40-5	d
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)-ethoxy]	55956-25-7	o	1,2-Propylene glycol n-propyl ether	1569-01-3, 30136-13-1	d
Propargyl alcohol	107-19-7	n	1,2-Propylene glycol dimethyl ether	7778-85-0	d,e
2-Propenenitrile	107-13-1	b,c,g,h,j,k,n	1,2-Propylen-imine	75-55-8	c,j,k,n
1-Propenyl benzene (ß-methyl styrene)	637-50-3	a,d,e	Pyridine	110-86-1	a,k,n
β-Propiolactone	57-57-8	c,e,j,k,n	Quinoline	91-22-5	j,k
Propionic acid	79-09-4	a,d,e,n,o	Quinone	106-51-4	j,n
2-Propoxyethanol	2807-30-9	d,e	Safrole, 5-allyl-1,3-benzo-dioxole	94-59-7	c,k
Propyl acetate	109-60-4	a,d,e,n	o-sec-Butylphenol	89-72-5	n
n-Propyl benzene	103-65-1	a,d,e	Stoddard solvent	8052-41-3	n
N-Propyl nitrate	627-13-4	n	Styrene	100-42-5	a,d,e,f,i,j,l,m, n,o
Propylene carbonate	108-32-7	d	Styrene oxide	96-09-3	c,g,h,j,k
Propylene glycol	57-55-6	a,d,e,o	p-tert-Butyl toluene	98-51-1	n
Propylene glycol diacetate	623-84-7	d,e	tert-Pentane	463-82-1	n

Table F-1 (contd.14) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
1,1,2,2-Tetrachloro-1,2-difluoroethane	76-12-0	n	2,4-Toluene diisocyanate	584-84-9	j,k,n,o
1,1,1,2-Tetrachloro-2,2-difluoroethane	76-11-9	n	o-Toluidine	95-53-4	c,g,h,j,k,n,o
1,1,1,2-Tetra-chloroethane	630-20-6	a	m-Toluidine	108-44-1	n
1,1,2,2-Tetra-chloroethane	79-34-5	a,j,k,n	p-Toluidine	106-49-0	n
Tetrachloro-ethene	127-18-4	a,e,f,i,j,k,n,o	Tributyl phosphate	126-73-8	d,e
Tetrachloro-naphthalene	1335-88-2	n	1,1,2-Trichloro-1,2,2-trifluoro-ethane	76-13-1	n
Tetrachloro-toluene	5216-25-1	c,h,k	1,2,4-Trichloro-benzene	120-82-1	j,n,o
n-Tetradecane	629-59-4	a,o	1,1,1-Trichloro-ethane	71-55-6	a,i,j,l,n,o
Tetrahydrofuran (THF)	109-99-9	a,d,n	1,1,2-Trichloro-ethane	79-00-5	a,j,k,n
1,2,3,5-Tetra-methyl benzene	527-53-7	o	Trichloroethene	79-01-6	a,c,f,g,h,i,j,k, n,o
1,2,4,5-Tetra-methyl benzene	95-93-2	a,d,e,o	Trichloro-naphthalene	1321-65-9	n
Tetramethyl succinonitrile	3333-52-6	n,o	2,4,5-Trichlorophenol	95-95-4	j
Tetranitro-methane	509-14-8	c,g,k,n	2,4,6-Trichlorophenol	88-06-2	j,k
Thioacetamide	62-55-5	c,k	2,4,5-Trichloro-phenoxyacetic acid	93-76-5	n
Thioglycolic acid	68-11-1	n	1,2,3-Trichloro-propane	96-18-4	c,g,h,k,n,o
Thiourea	62-56-6	k	n-Tridecane	629-50-5	a,o
o-Tolidine	119-93-7	c,g,h,j,k	Triethanolamine	102-71-6	n
Toluene	108-88-3	a,d,e,f,i,j,k, l,m,n,o	Triethyl phosphate	78-40-0	d,e

Table F-1 (contd.15) Chemicals occurring on one or more lists of target compounds

Compound	CAS No.	List(s) on	Compound	CAS No.	List(s) on
Triethylamine	121-44-8	d,e,j,n,o	Tripropylene glycol-monomethyl ether	20324-33-8 25498-49-1	d,e
Triethylene glycol dimethyl ether	112-49-2	d,e	Tris(2-chloro-ethyl) phosphate	115-96-8	k
Trimethyl benzene	25551-13-7	n,o	Turpentine	8006-64-2	a
Trimethyl phosphate	512-56-1	k,o	n-Undecane	1120-21-4	a,o
2,2,4-Trimethyl-1,3-pentanediol-isobutyrate	25265-77-4	a,d,e,o	2-Undecenal	2463-77-6, 53448-07-0	a,d,e
2,4,5-Trimethyl-aniline	137-17-7	c,h,k	n-Valeric acid	109-52-4	a,d,e
1,3,5-Trimethyl-benzene	108-67-8	a,d,e,n	Vinyl acetate	108-05-4	a,d,i,j,m,n,o
1,2,3-Trimethyl-benzene	95-63-6	a,d,e,n	Vinyl toluene (all isomers: o-, m-, p-methyl styrenes)	25013-15-4, 100-80-1, 622-97-7, 611-15-4	a,d,e,n
1,2,4-Trimethyl-benzene	526-73-8	a,d,e,f,n	4-Vinyl-1-cyclohexene diepoxide	106-87-6	c,k,n
3,3,5-Trimethylcyclo-hex-2-enone	78-59-1	a,i,j,n,o	N-Vinyl-2-pirrolidinone	88-12-0	n
2,4,6-Trimethyloctane	62016-37-9	a	4-Vinyl-cyclohexene	100-40-3	k,m,n,o
2,2,4-Trimethyl-pentane	540-84-1	j,n,o	o-Xylene	106-42-3	a,d,i,j,n,o
2,2,4-Trimethyl-pentanedioldiiso-butyrate (TXIB)	6846-50-0	a,d,e	m-Xylene	108-38-3	a,d,i,j,n,o
2,4,6-Trinitrophenyl-methylnitramine	479-45-8	n	p-Xylene	95-47-6	a,d,i,j,l,n,o
2,4,6-Trinitro-toluene	118-96-7	k	Xylene, mix of o, m- and p-xylene isomers	1330-20-7	d,e,f,j,m,n,o
Triphenylamine	603-34-9	n	m-Xylylene-diamine	1477-55-0	n

F.2 List of chemicals analysed on TD-100/GC/MSD system

Table F-2 List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)														
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
4.18	Acetaldehyde	75-07-0	21	7	N	Aldrich	SQ	Y	Y		V	Y	Y			Y	Y	Y		Y	Y	Y
4.66	Ethanol	64-17-5	78	4	I, N	Aldrich	5-1000				V											
5.09	Acetonitrile	75-05-8	82	12		Aldrich	25-1000										Y					
5.10	Acetone	67-64-1	56	8	I, N	Fisher	5-1000	Y			V											
5.15	2-Propanol	67-63-0	82	4	I	Supelco	5-1000	Y			V					Y					Y	Y
5.21	n-Pentane	109-66-0	36	2		BDH	5-500															
5.36	Isoprene	78-79-5	34	2	N	Aldrich	5-600											Y				
5.64	2-methyl-2-propanol	75-65-0	82	4		Aldrich	SQ	Y			Y	Y									Y	
5.65	Acrylonitrile	107-13-1	77	12		Aldrich	5-250		Y	Y				Y	Y		Y	Y			Y	
5.80	Dichloromethane	75-09-2	40	11	I, N	Acros	5-1000	Y	Y							Y	Y	Y			Y	Y
5.96	Carbon disulphide	75-15-0	46	12		Aldrich	SQ									Y	Y	Y			Y	Y
6.28	1-Propanol	71-23-8	97	4	I	Aldrich	5-1000	Y			V										Y	
6.61	Tert-butylmethylether	1634-04-4	55	12	N	Aldrich	5-750									Y	Y				Y	
6.92	Vinyl acetate	108-05-4	72	10	N	Aldrich	5-1000				V					Y	Y			Y	Y	Y
7.25	2-Butanone	78-93-3	80	8	I	Aldrich	5-1000	Y			Y	Y					Y				Y	Y
7.37	n-Hexane	110-54-3	69	2	C, I	BDH	5-750	Y			Y	Y				Y	Y		Y		Y	Y
7.38	sec-Butanol	78-92-2	98	4		Acros	SQ				O										Y	Y
7.61	Acetic acid	64-19-7	117	9		Fisher	SQ	Y			Y	Y									Y	

Table F-2 (contd.1) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)														
								a	b	c	d	e	f	g	h	i	j	K	l	m	n	o
7.85	Ethyl acetate	141-78-6	77	10	I, N	Fluka	5-1000	Y			V					Y					Y	Y
8.02	Chloroform	67-66-3	61	11	I, N	Supelco	5-1000									Y	Y	Y			Y	
8.31	2-methyl-1-propanol	78-83-1	108	4		Aldrich	SQ	Y			Y	Y									Y	Y
8.38	2,4-Dimethylpentane	108-08-7	81	2	I	Supelco	5-1000				A	A										
8.41	Tetrahydrofuran (THF)	109-99-9	67	12	N	Aldrich	5-1000	Y			Y										Y	
8.55	2-methoxyethanol	109-86-4	125	6		Aldrich	SQ	Y	Y		Y	Y				Y	G	Y			Y	Y
9.20	1,2-Dichloroethane	107-06-2	84	11	I	Supelco	5-1000	Y		Y				Y	Y		Y	Y			Y	Y
9.44	1,2-Dimethoxyethane	110-71-4	85	6		Acros	5-1000	Y			Y	Y					G					
9.74	1-Butanol	71-36-3	117	4	I	Supelco	5-1000	Y			Y	Y							Y		Y	Y
9.81	Benzene	71-43-2	80	1	I	Fisher	5-1000	Y	Y	Y			Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
9.83	Carbon tetrachloride	56-23-5	76	11		BDH	SQ	Y				Y				Y	Y	Y			Y	
9.87	Cyclohexane	110-82-7	81	2		Acros	5-750	Y			Y	Y							Y		Y	Y
10.91	Triethylamine	121-44-8	89	12		Aldrich	5-750				Y	Y					Y				Y	Y
10.98	2,2,4-Trimethylpentane	540-84-1	99	2	I	Supelco	5-1000				A	A					Y				Y	Y
11.21	Ethylene glycol	107-21-1	197	6		Aldrich	150-2000				Y	Y				Y	Y				Y	Y
11.46	Ethyl acrylate	140-88-5	99	10		Fluka	5-1000	Y			Y	Y					Y	Y			Y	
11.54	1,2-Dichloropropane	78-87-5	96	11	I	Supelco	5-1000										Y	Y			Y	Y
11.55	Bromodichloromethane	75-27-4	87	12	I	Supelco	5-1000											Y				
11.56	1,4-Dioxane	123-91-1	101	12		Fluka	5-1000	Y	Y		Y	Y				Y	Y	Y			Y	Y
11.58	n-Heptane	142-82-5	98	2	I	Supelco	5-1000	Y			Y	A									Y	Y

Table F-2 (contd.2) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)															
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
11.60	Trichloroethylene	79-01-6	87	11	I	Supelco	5-1000	Y		Y			Y	Y	Y	Y	Y	Y			Y	Y
12.23	2-ethoxyethanol	110-80-5	135	6		Sigma	SQ	Y	Y		Y	Y				Y	G	Y			Y	Y
12.24	Methyl methacrylate	80-62-6	100	10		Fluka	5-1000	Y			Y	Y					Y				Y	Y
13.46	Isoamyl alcohol	123-51-3	131	4		Aldrich	SQ				P	P									Y	
13.85	4-Methylpentan-2-one (MIBK)	108-10-1	117	8	C, I	Aldrich	5-1000	Y			Y	Y					Y		Y		Y	Y
14.07	Pyridine	110-86-1	116	12		Aldrich	10-1000	Y										Y			Y	
15.48	d8-toluene (IS)	2037-26-5	110	1		Supelco	IS															
15.78	Toluene	108-88-3	111	1	C, I	Aldrich	5-1000	Y			Y	Y	Y			Y	Y	Y	Y	Y	Y	Y
16.52	Dimethylformamide (DMF)	68-12-2	153	12		Riedel de Haen	34-1000				Y					Y	Y				Y	Y
17.86	Hexanal	66-25-1	129	7	C	Aldrich	7-1000	Y			Y	Y							Y			
17.99	n-Octane	111-65-9	125	2	I	Supelco	5-1000	Y			A	A									Y	
18.30	Butanoic acid	107-92-6	163	9		Aldrich	SQ	Y			Y	Y										
18.39	1,2-Dibromoethane	106-93-4	132	12		Acros	SQ			Y				Y	Y		Y	Y			Y	
18.85	Tetrachloroethylene	127-18-4	121	11	I	Supelco	5-1000	Y			Y	Y	Y			Y	Y	Y			Y	Y
18.97	Butyl acetate	123-86-4	126	10	C, I	Aldrich	5-1000	Y			Y	Y							Y		Y	Y
20.22	Furfuraldehyde	98-01-1	162	7		Aldrich	SQ	Y			Y	Y									Y	Y
20.92	Diacetone alcohol	123-42-2	166	4		Aldrich	5-1000				Y	Y									Y	Y
22.40	Acrylamide	79-06-1	125	12		Sigma	SQ		Y	Y					Y		Y	Y			Y	
22.66	Ethylbenzene	100-41-4	135	1	I	Supelco	5-1000	Y			Y	Y	Y			Y	Y	Y	Y		Y	Y
22.90	1-methoxy-2-propylacetate	108-65-6	146	6		Acros	SQ				Y	Y									Y	Y

Table F-2 (contd.3) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)														
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
23.15	4-heptanone	123-19-3	145	8		Aldrich	SQ														Y	
23.20	m/p-Xylene	108-38-3/ 106-42-3	137	1	I	Aldrich	5-1000	Y			Y	X	Y			Y	Y		Y	Y	Y	Y
24.58	Styrene	100-42-5	144	1	I	Supelco	5-1000	Y			Y	Y	Y			Y	Y		Y	Y	Y	Y
24.65	Cyclohexanone	108-94-1	155	8	C	Aldrich	5-1000	Y			Y	Y									Y	Y
24.66	1,3-dichloro-propan-2-ol	96-23-1	174	11		Aldrich	5-500			Y				Y	Y							Y
24.72	Butyl acrylate	141-32-2	145	10		Fluka	5-1000				Y	Y									Y	Y
24.76	o-Xylene	95-47-6	144	1	I	Supelco	5-1000	Y			Y	X	X			Y	Y			X	Y	Y
24.94	Pentanoic acid	109-52-4	186	9		Aldrich	SQ	Y			Y	Y										
25.08	n-Nonane	111-84-2	149	2	I	Supelco	5-1000	Y			H	H									Y	Y
25.32	2-Butoxyethanol	111-76-2	171	6		Aldrich	10-1000	Y			Y	Y	Y				G		Y		Y	Y
27.25	(1S)-(-)α-Pinene	80-56-8	156	3	I	Supelco	5-1000	Y			Y	Y							Y		Y	Y
27.98	2-ethylhexanal	123-05-7	163	7		Fluka	SQ	Y			Y	Y										
28.44	Benzaldehyde	100-52-7	179	7		Aldrich	SQ	Y			Y	Y										
28.58	3-Ethyltoluene	620-14-4	158	1	I	Supelco	5-1000	E														
28.66	4-Ethyltoluene	622-96-8	161	1	I	Supelco	5-1000	E														
28.93	2-Ethyltoluene	611-14-3	164	1	I	Supelco	5-1000	Y			Y	Y										
29.25	Phenol	108-95-2	182	5	C	Acros	21-1000	Y			Y	Y				Y	Y			Y	Y	Y
29.51	(−)-β-Pinene	18172-67-3	166	3	I	Supelco	5-1000	Y			Y	Y										Y
29.52	Mesitylene	108-67-8	165	1	I	Supelco	5-1000	Y			Y	Y									Y	

Table F-2 (contd.4) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)															
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
30.18	1,2,4-Trimethylbenzene	95-63-6	168	1	I	Supelco	5-1000	Y			Y	Y	Y								Y	
30.29	n-Decane	124-18-5	173	2	I	Supelco	5-1000	Y			H	H							Y			
30.38	2-(2-Ethoxyethoxy)-ethanol	111-90-0	202	6		Aldrich	5-1000				Y	Y					G					
31.01	Benzyl chloride	100-44-7	179	11		Aldrich	5-500			Y				Y	Y		Y	Y			Y	
31.05	1,4-Dichlorobenzene	106-46-7	174	11	I	Supelco	5-1000	Y					Y			Y	Y				Y	Y
31.49	2-Ethylhexan-1-ol	104-76-7	183	4		Aldrich	5-1000	Y			Y	Y								Y		Y
31.53	1,2,3-Trimethylbenzene	526-73-8	176	1	C, I	Aldrich	5-1000	Y			Y	Y									Y	
31.78	(*R*)-(+)-Limonene	138-86-3	176	3	I	Aldrich	5-1000	Y			Y	Y										Y
32.03	N-methyl-2-pyrrolidinone	872-50-4	202	12		Aldrich	SQ	Y			Y	Y						Y		Y		Y
33.20	Octan-1-ol	111-87-5	196	4		BDH	5-1000	Y			Y	Y										
33.22	p-Cresol	106-44-5	202	5		Aldrich	SQ										Y					Y
33.46	o-Toluidine	95-53-4	200	12		Aldrich	5-500			Y				Y	Y		Y	Y			Y	Y
33.84	2-Butoxyethyl acetate	112-07-2	192	6		Aldrich	5-1000	Y			Y	Y									Y	
34.40	n-Undecane	1120-21-4	195	2	I	Supelco	5-1000	Y			H	H										Y
34.54	Nonanal	124-19-6	191	7	I	Supelco	5-1000	Y			Y	Y								Y		Y
35.12	2-Ethylhexanoic acid	149-57-5	222	9		Aldrich	30-1000				Y	Y						Y		Y	Y	Y
35.21	1,2,4,5-Tetramethyl-benzene	95-93-2	196	1	I	Supelco	5-1000	Y			Y	Y										Y

Table F-2 (contd.5) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)															
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
36.67	Octanoic acid	124-07-2	240	9		Aldrich	SQ	Y			Y	Y											
36.93	o-Anisidine	90-04-0	225	12		Aldrich	10-500			Y				Y	Y		Y	Y			Y	
37.04	2-(2-Butoxyethoxy)-ethanol	112-34-5	231	6		Aldrich	30-1000	Y			Y	Y					G					Y
37.38	n-Dodecane	112-40-3	215	2	I	Aldrich	5-750	Y			H	H							Y			Y
37.43	Naphthalene	91-20-3	218	1		Aldrich	5-1000	Y			Y	Y				Y	Y	Y		Y	Y	Y
37.53	Decanal	112-31-2	208	7	I	Supelco	5-1000	Y			Y	Y										Y
37.72	4-Chloroaniline	106-47-8	232	12		Aldrich	10-1000			Y				Y	Y			Y				
39.61	n-Tridecane	629-50-5	235	2	I	Supelco	5-1000	Y			H	H										Y
40.72	4-Phenylcyclohexene	4994-16-5	243	1	C	TCI	5-300	Y			Y	Y						Y		Y		Y
40.8, 41.3	2,2,4-Trimethyl-pentanediolmono-isobutyrate (Texanol)	25265-77-4	255	6		Sigma	5-500	Y			Y	Y										Y
41.41	n-Tetradecane	629-59-4	253	2	I	Supelco	5-1000	Y			H	H										Y
41.52	Biphenyl	92-52-4	255	1		Fisher	5-350										Y				Y	
42.50	Dimethyl phthalate	131-11-3	217	12		Aldrich	SQ	Y									Y				Y	
42.54	Diethanolamine	111-42-2	217	12		Aldrich	SQ										Y				Y	
42.71	Butylated hydroxy-anisole (BHA)	25013-16-5	264	12		Acros	5-300											Y				
42.94	n-Pentadecane	629-62-9	270	2	I	Supelco	5-1000	Y			H	H										Y

Table F-2 (contd.6) List of chemicals analysed on TD-100/GC/MSD system

Retention Time (min)	Compound	CAS No.	Boiling point (°C)	Compound Type [1]	in mix(es) C, I and/or N [2]	Source	Quantification range (ng) / SQ [3]	Target list (for index see Table 2-1)															
								a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
43.41	Butylated hydroxytoluene (BHT)	128-37-0	265	5	C	Sigma	5-300	Y			Y	Y									Y	Y
44.30	n-Hexadecane	544-76-3	285	2	C, I	Aldrich	5-300	Y			H	H										
44.44	Diethylphthalate	84-66-2	298	12		Aldrich	5-400														Y	
44.46	2,2,4-Trimethylpent-anedioldiisobutyrate (TXIB)	6846-50-0	280	6		Aldrich	5-300	Y			Y	Y										
44.93	Tributyl phosphate	126-73-8	289	12		Aldrich	SQ				S	Y										
46.68	n-Octadecane	593-45-3	317	2		Aldrich	SQ				H	H										
47.64	Diisobutyl phthalate	84-69-5	320	10		Aldrich	SQ															
47.81	Dodecyl benzene	123-01-3	331	1		Koch Light	5-1000				B											
48.34	Hexadecanoic acid	57-10-3	350	9		Aldrich	SQ	Y														
48.62	Dibutyl phthalate	84-74-2	340	10		Aldrich	5-400	Y					Y				Y	Y				
54.90	Bis-2-ethylhexyl-phthalate (DEHP)	117-81-7	384	10		Aldrich	5-300						Y				Y	Y				
Total calibrated (not including extra compounds combined on a list)								78	8	11	63	59	13	10	11	27	43	33	15	13	72	64
Number of compounds in list								167	14	97	176	165	14	38	54	35	128	192	16	20	316	119
% of compounds in list calibrated								47	57	11	36	36	93	26	20	77	33	17	94	65	23	54

Key to Table F-2 (see Table 2-1 for details of target compound lists):

[1] − Compound type as defined in list d (AgBB scheme)

[2] – 'C' is the 11 compound check standard mix (see Section 1.4.1); 'I' is the Supelco 50 compound indoor air mix and 'N' is the mixture of VVOCs tested using Nalopan bags (Section 5.2.1.3).

[3] – this is the quantification range achieved using the minimum split ratio on the TD-100 and full scan ionisation mode for the MSD. Lower amounts may be determined by use of selected ion monitoring mode on the MSD or TOF MS and greater amounts can be quantified by using a TD method with a bigger split ratio; SQ or 'semi-quant' denotes a compound which has been quantified using the calibration factor for toluene

A − combined on lists d and e (AgBB and AFSSET) as 'saturated aliphatic hydrocarbons, up to C8'

B – combined on AgBB list as 'other alkylbenzenes

E − 3-ethyltoluene and 4-ethyltoluene combined on list a (ISO 16000-6:2011)

G – combined on list j as 'glycol ethers' (TAC list)

H − combined on lists d and e (AgBB and AFSSET) as 'saturated hydrocarbons C9 or higher'

O − combined on list d (AgBB) as 'other saturated n- and iso- alcohols, C4-C10'

P – combined on lists d and e (AgBB and AFSSET) as 'pentanol (all isomers)'

S − Classified on list d (AgBB) as a SVOC and no LCI value set

V − Classified on list d (AgBB) as a VVOC and "not currently considered in the AgBB evaluation scheme"

X − Xylene isomers combined on several lists

Y − Included on list.

Appendix G Publications resulting from the project

G.1 Journal papers

Veronica M. Brown and Derrick R. Crump, 'An investigation into the performance of a multi-sorbent sampling tube for the measurement of VVOC and VOC emissions from products used indoors', Analytical Methods, 2013, 5, 2746-2756, DOI: 10.1039/C3AY40224J

Veronica M. Brown, Derrick R. Crump, Neil T. Plant and Ian Pengelly, 'Evaluation of a mixture of volatile organic compounds on sorbents for the determination of emissions from indoor materials and products using TD/GC/MS', drafted for submission to Journal of Chromatography A, 2013.

G.2 Conference paper presented orally

Veronica Brown and Derrick Crump, 'Improved methods for the screening of building and furnishing materials for VOC emissions', in proceedings of the 10th International Healthy Buildings conference, 8-12 July 2012, Brisbane, Australia, Paper No: 4.B.2.

G.3 Conference papers presented as posters

Veronica Brown and Derrick Crump, 'The Use of Screening Tests to Determine Emissions of VOCs from Building and Furnishing Materials', in: Indoor Air: Proceedings of the 12th International Conference on Indoor Air Quality and Climate, 5-10 June 2011, Austin, Texas, Paper No: 752

Veronica Brown and Derrick Crump, 'Optimisation of analytical parameters for the determination of VOCs emitted by construction and consumer products', in: Proceedings of the 2011 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 10-11 May 2011, IEH, Cranfield University, UK, web report W29, p.141-145, available at http://www.cranfield.ac.uk/about/people-and-resources/schools-and-departments/school-of-applied-sciences/groups-institutes-and-centres/ieh-reports-/air-pollution/w29.pdf

Veronica Brown and Derrick Crump, 'Application of multi-sorbent tubes and data analysis software to the determination of VOCs released from building materials', in: Proceedings of the 2012 Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research, 3-4 May 2012, IEH, Cranfield University, UK, web report 31, p. 117-121, available at http://www.cranfield.ac.uk/about/people-and-resources/schools-and-departments/school-of-applied-sciences/groups-institutes-and-centres/ieh-reports-/air-pollution/w31.pdf.